DEVELOPMENTS IN
MINERAL PROCESSING
15

ADVANCES IN GOLD ORE PROCESSING

EDITED BY
M.D. ADAMS

SERIES EDITOR: B.A. WILLS

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ADVANCES IN GOLD ORE PROCESSING

Mike D. Adams
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series editor: B.A. Wills

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Preface

The gold-processing industry is experiencing change. As free-milling and oxide ores become depleted, more complex polymetallic and refractory ores are being processed, coupled with increasing pressure for stricter environmental compliance. Recent years have also seen a steady reduction in mineral processing and metallurgy graduates and a gradual loss of older operating experience. A contribution to documenting current and future best practice in gold ore processing seems timely.

The focus of this volume is on advances in current gold plant operation, from conception to closure; each chapter also covers recent innovations at the bench and pilot-scale level that would be expected to find commercial application at some stage. A coverage of essential chemistry and engineering aspects is included.

Part I of the book focuses on project development, with an emphasis on the various aspects of feasibility study management and taking the path through commissioning, safety and environmental management in operation, and finally closure of both plant and tailings storage facility. With increasing pressures on the resource company to ensure minimal socio-environmental impact through the entire life cycle of the mine, it is important to aim at getting it 'right first time'.

Part II centres on the process plant, sequentially probing the generic gold-processing flowsheet for advances, best practice and potential future practical innovations. This is the heart of the book; there is coverage of the various unit operations involved with comminution, concentration, oxidation, leaching, gold recovery and disposal of residues and effluents. Innovations described in the comminution chapter include those undertaken at Freeport, which is one of the largest gold mill in the world (despite being a copper mine). Concentration of gold by gravity has seen innovation driven partly by the development of new items of equipment, and novel application within the milling circuit, such as is now commonplace in areas such as Western Australia. Flotation has similarly been influenced by the advent of flash and column flotation, as well as the application of differential floats for complex ores.

Treatment of refractory ores has necessarily become increasingly important, and the section covering pressure and bacterial oxidation as well as roasting (both oxygenated and fluidized bed) has particular relevance to the modern gold metallurgist. While these technologies can now be deemed as established, the recent advances outlined in the book are clearly both novel and practical. Development of methods that increase recoveries while decreasing reagent consumption by minimizing cyanicide formation are clearly at the forefront of these areas and further development is certain.

Again in the leaching section the emphasis is on treatment of problematic ores such as those arising from oxidation processes. There has been a drive in recent years towards the development of alternative lixiviants for gold, mainly as a result of environmental pressures. The most likely candidate for niche application is thiosulfate leaching; the amount of recent work in this area has warranted inclusion of this topic as a separate chapter. Cyanide has seen practical application for over 100 years now, and this will continue, with the ongoing positive initiatives in cyanide management such as the Cyanide Code (which has also warranted a chapter in its own right) and the inherent benefits of a reagent that, in a well-designed flowsheet, is low level and biodegradable.

Advances in the recovery of gold from leach solution are again influenced by developments in equipment and reagents. Ongoing improvements in the refining of gold are also being made. Innovations such as the Anglo American Corporation (AAC) pump cell contactor and gold-selective resin-in-pulp have found niche application at a few operating plants. The extent of their use will depend on a number of factors, but the trend towards polymetallic and refractory ores is likely to open up new applications that may require some innovative flowsheeting if the base-metal and precious-metal values are both to be economically recovered.

There is another area that has a positive bearing on the future of cyanide in gold processing. The application of cyanide detoxification or recovery processes into flowsheets is becoming much more prevalent. This may well again reflect an increasing sense of environmental stewardship by resource companies, undoubtedly driven by the need for the two prongs of public and operator perception to meet in a common reality. A number of new technologies for the economic recovery and recycle of cyanide from plant tailings have now been developed, and this may well be a key element to the ongoing responsible use of cyanide. Perhaps the main area where public perception has been negatively influenced has been with tailings storage facilities. Placement of paste or dry tailings using techniques such as centrally thickened discharge, for example, is an innovation that addresses issues of dam stability and water recovery, whilst resulting in a more natural-looking landform on closure.

Part III assesses the principles and developments outlined in the first two parts, by means of focused case studies of typical flowsheets for the two major types of problematic gold ores that are being encountered – polymetallic and refractory ores. A distinction is made on economic grounds between gold–copper ores and copper–gold ores; process flowsheets and issues differ between the two. Ores containing high silver, base-metal and platinum-group metal (PGM) grades will continue to be more often in resource companies' fields of view as the quest for paydirt continues. As orebodies become more complex, so too do the process flowsheets, with an increasing reliance on hydrometallurgical treatments that result in a variety of products, not only gold but also copper, nickel, cobalt, silver, PGMs and sometimes lead and zinc.

While refractory sulfides have been around for some time, an understanding is being gained of the subtle chemistry that can arise in high-pressure autoclaves treating a sometimes extensive mix of different sulfide minerals. As both the knowledge base and the number of applications increase, so the risk of applying these processes becomes smaller. The same can be said of other problematic ores, such as carbonaceous preg-robbing, tellurides and antimonial ores.

The general principle behind the structure of the volume is that of flowsheeting based on unit operations and applied to a mineralogical classification of gold ore types. Knowledge of the mineralogy of an orebody is the key to unlocking the wealth contained within. The extensive chapter covering this aspect necessarily does so through process eyes; flowsheet definition can then follow using the building blocks comprising the unit operations described in the second part of the volume.

Practical experience is vital to the successful development, operation and closure of any operation. The 42 chapters have been contributed by a total of 66 authors and co-authors who are experts from countries spanning the globe, and representing exhaustive practical knowledge covering many disciplines relevant to gold processing. Within the chapters are numerous tidbits of practical personal experience, much of which is as yet unpublished. The content will be useful to operators, engineers and researchers worldwide.

The original intention was to provide a selection of appendices covering SI units, conversion factors, pulp density tables and the like. The ready availability of this information on the internet has made their inclusion redundant; however, a Periodic Table kindly made available by Prof. Fathi Habashi has been included.

This book is intended for mineral-processing engineers, metallurgists, process mineralogists, mining engineers, environmental engineers and consultants, as well as resource company managers. It will be of interest to professionals and students alike.

M.D. Adams

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List of Acronyms

μ-PIXE	micro-particle-induced X-ray emission
AAC	Anglo American Corporation
AARL	Anglo American Research Laboratories
ABA	Acid–base accounting
AC	activated carbon
AGC	Ashanti Goldfields Company
AI	abrasion index
AIA	automated image-analysis
AIChE	American Institute of Chemical Engineers
AIME	American Institute of Mining, Metallurgical, and Petroleum Engineers
AMD	acid mine-drainage
ANC	acid neutralizing capacity
ANFO	ammonium nitrate and fuel oil
ASTM	American Society for Testing and Materials (now ASTM International)
AusIMM	Australasian Institute of Mining and Metallurgy
AVR	Acidification–volatilisation–regeneration
AWWA	American Water Works Association
BBMWI	Bond ball-mill work index
BGMI	Barrick Goldstrike Mines
BRMWI	Bond rod-mill work index
BSE	back-scattered electron
BTAC-CIL	bench-top autoclaving followed by carbon-in-leach
CAPEX	capital expenditure
CCD	counter-current decantation
CCTV	closed-circuit television
CESL	Cominco Engineering Services Limited
CFB	circulating fluidized bed
CFD	computation fluid dynamics
CIL	carbon-in-leach
CIM	Canadian Institute of Mining, Metallurgy and Petroleum
CIP	carbon-in-pulp
CIS	carbon-in-solution
CIS	Commonwealth of Independent States
CMC	carboxy-methylcellulose
CPS	controlled-potential sulfidization
CSTR	continuous stirred-tank reactor
CTC	carbon-tetrachloride activity
CTD	centrally thickened discharge
CWI	crushing work index

DCS	distributed control system
DO	dissolved oxygen
DPO	dynamic process optimization
DR	direct reduction
EDS	energy-dispersive spectrometry
EDX	energy-dispersive X-ray analysis
EFA	ecosystem function analysis
EPC	engineering, procurement and construction
EPCM	engineering, procurement and construction management
EPMA	electron-probe microanalysis
ESP	electrostatic precipitator
EU	European Union
EW	electrowinning
FAG	fully autogenous grinding
FB	fluidized bed
FTIR	Fourier-transform infrared spectroscopy
GGFL	Gekko gravity-float-leach
GPS	global positioning system
GRG	gravity-recoverable gold
HAZOP	hazard and operability study
HDPE	high-density polyethylene
HMSO	Her Majesty's Stationery Office
HOPG	highly organized pyrolytic graphite
HPGR	high-pressure grinding rolls
HR-TEM	high-resolution transmission electron microscopy
HSGE	high-speed gold-electrolysis
HSSE	high-speed silver-electrolysis
ICME	International Council on Metals and the Environment
ICMI	International Cyanide Management Institute
ICOLD	International Commission on Large Dams
IEP	isoelectric point
ILR	Inline Leach Reactor
IMM	Institute of Mining and Metallurgy
IPMI	International Precious Metals Institute
IPS	integrated pressure strip
IR	industrial relations
ISO	International Standards Organization
LBMA	London Bullion Market Association
L-ICP-MS	laser inductively coupled-plasma mass-spectrometry
LME	London Metal Exchange
LPG	liquid petroleum gas
LSTK	Lump-sum turn key
MAC	magnetic activated carbon
MAC	Mining Association of Canada
MBT	mercaptobenzothiozole

MCC	Motor Control Centre
MGS	Mozley Gravity Separator
MIBC	methyl isobutyl carbinol
MIBK	methyl *iso*butyl ketone
MLS	Mozley Laboratory Separator
MNR	Metallgesellschaft natural resources
MPA	maximum potential acidity
MPC	model predictive control
NAG	net acid generation
NAPP	net acid-producing potential
NHE	normal hydrogen electrode
NPV	net present value
NRS	net smelter return
OCS	optimizing control systems
OPEX	operating expense
ORP	oxidation–reduction potential
OSA	optical spectrum analyser
OT	Outokumpu Technology
PAX	potassium amyl xanthate
PC	personal computer
PGMs	platinum-group metals
PI	proportional-integral (feedback control-loops)
PIXE	particle-induced X-ray emission
PLC	programmable logic controller
PLS	pregnant leach solution
POX	pressure oxidation
PSA	pressure-swing adsorption
PSD	particle-size distribution
PTFI	PT Freeport Indonesia
QA	quality assurance
RBC	rotating biological contactor
REQCM	rotating electrochemical quartz-crystal microbalance
RIL	resin-in-leach
RIP	resin-in-pulp
RIS	resin-in-solution
RLE	roast-leach-electrowinning
ROM	run-of mine
SAG	semi-autogenous grinding
SAIMM	South African Institute of Mining and Metallurgy
SALI	surface analysis by laser ionization
SART	sulfidization-acidification-recycling-thickening
SCR	selective catalytic reduction
SDGM	Sunrise Dam Gold Mine
SEM	scanning electron microscopy
SEM/EDX	scanning electron microscopy/energy-dispersive X-ray analysis

SET	silver-enhancement treatment
SG	specific gravity
SHE	standard hydrogen electrode
SIBX	sodium *iso*butyl xanthate
SIMS	secondary-ion mass spectrometry
SLS	sodium lauryl sulfate
SME	Society for Mining, Metallurgy and Exploration
SX	solvent extraction
TCLP	toxicity characteristics leaching procedure
TCM	total carbonaceous matter
TDS	total dissolved solids
TLV	threshold limiting value
TMS	The Minerals, Metals and Materials Society
TOF-LIMS	time-of-flight laser-ionization mass spectrometry
TOF-RIMS	time-of-flight resonant-ionization mass spectrometry
TOF-SIMS	time-of-flight secondary-ion mass spectrometry
TSF	tailings storage facility
UBC	University of British Columbia
UCS	unconfined compressive strength
UFG	ultra-fine grinding
UFM	ultra-fine milling
UNEP	United Nations Environment Programme
US EPA	United States Environmental Protection Agency
USMR	US Metals Refining
VAW	Vereinigte Aluminium Werke
VUV	vacuum ultra-violet
VUV-TOF-LIMS	vacuum ultra-violet TOF-LIMS
WAD	weak-acid dissociable (cyanide)
WDX	wavelength-dispersive X-ray analysis
WHO	World Health Organization
XANES	X-ray absorption near-edge structure spectroscopy
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffractometry

List of Mineral Formulae

acanthite	Ag_2S
altaite	$PbTe$
alumina	Al_2O_3
argentojarosite	$Ag_2Fe_3(SO_4)_4(OH)_{12}$
arsenian pyrite	$AsFeS_2$
arsenopyrite	$FeAsS$
auricupride	Cu_3Au
auroantimonate	$AuSbO_3$
aurostibite	$AuSb_2$
azurite	$2Cu(CO)_3 \cdot Cu(OH)_2$
bassanite	$CaSO_4 \cdot \frac{1}{2}H_2O$
berthierite	$FeSb_2S_4$
bezsmertnovite	$Au_4Cu(Te,Pb)$
bogdanovite	$Au_5(Cu,Fe)_3(Te,Pb)_2$
bornite	$FeS \cdot 2Cu_2S \cdot CuS$
braggite	PtS
calaverite	$AuTe_2$
chalcocite	Cu_2S
chalcopyrite	$CuFeS_2$
chlorargyrite (cerargyrite)	$AgCl$
chlorite	$(Mg,Al,Fe)_{12}[(Si,Al)_8O_{20}](OH)_{16}$
chrysocolla	$CuSiO_3 \cdot nH_2O$
cinnabar	HgS
coloradoite	$HgTe$
cooperite	$(PtPdNi)S$
cordierite	$Mg_2Al_4Si_5O_{18}$
corundum	$Al_6Si_2O_{13}$
covellite	CuS
cuprite	Cu_2O
dolomite	$CaMg(CO_3)_2$
electrum	(Au,Ag); 20–80% molar Ag
enargite	Cu_3AsS_4
fayalite	Fe_2SiO_4
ferrous pyroarsenite	Fe_2AsO_5
fischesserite	Ag_3AuSe_2
galena	PbS
goethite	$FeO(OH)$
goldamalgam	$(Au,Ag)Hg$
gudmundite	$FeSbS$
gypsum	$CaSO_4 \cdot 2H_2O$
hematite	Fe_2O_3

hessite	Ag_2Te
hunchinite	Au_2Pb
iodargyrite	AgI
iridic gold	(Au,Ir)
jarosite	$H_3OFe_3(SO_4)_2(OH)_6$
kostovite	$CuAuTe_4$
kotulskite	$(PtPdNi)(TeBiSb)_2$
krennerite	$(Au,Ag)Te_2$
laurite	$(RuFeOsIrPt)S_2$
litharge	PbO
loellingite	$FeAs_2$
maghemite	Fe_2O_3 with $<5\%$ FeO
magnetite	Fe_3O_4
malachite	$2CuCO_3(OH)_2$
maldonite	Au_2Bi
marcasite	FeS_2
moncheite	$(PtPdNi)(TeBiSb)_2$
montbrayite	$(AuSb)_2Te_3$
mullite	$Al_6Si_2O_{13}$
muthmannite	(Au,Ag)Te
nagyagite	$[Pb(Pb,Sb)S_2][Au,Te]$
native copper	Cu
native gold	Au ($<20\%$ molar Ag)
orpiment	As_2S_3
palladian gold (porpezite)	(Au,Pd)
pentlandite	$(Fe,Ni)_9S_8$
petrovskaite	AuAg(S,Se)
petzite	Ag_3AuTe_2
platinum gold	(Au,Pt)
Pt–Fe alloys	Pt_3Fe
pyrite	FeS_2
pyrophyllite	$AlSi_2O_5OH$
pyrrhotite	$Fe_{1-x}S$
realgar	AsS
rhodian gold (pyrite)	(Au,Rh)
sphalerite	(Zn,Fe)S
stibnite	Sb_2S_3
sylvanite	$(Au,Ag)Te_2$
tetra-auricupride	AuCu
tetrahedrite	$(Cu,Fe,Ag,Zn)_{12}Sb_4S_{13}$
thucholite	variable mixture of hydrocarbons, uraninite and sulfides
uraninite	UO_2
uytenbogaardite	Ag_3AuS_2
weishanite	$(Au,Ag)_3Hg_2$
zincblende	ZnS

Gold – An historical introduction

F. Habashi

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1. GOLD IN ANCIENT EGYPT

From ancient times to the present day gold has been valued by man. Egypt was the principal gold-producing country in ancient times. Coptos, the present Quft on the eastern side of the River Nile, was the chief town of the Nomos of Harawi and was once politically important, but under the eleventh dynasty (2133–1991 BC) it was overshadowed by Thebes, 50 km to the south, which became the capital of the Middle Kingdom (2133 BC) of ancient Egypt, the present day Luxor (see Fig. 1). Coptos was the world's first gold boom town. It was there in the Wadi Hammamat that alluvial gold had been washed down from the gold-bearing veins found later in the granite hills above. The world's oldest mine map, which is made on papyrus and held at the Turin Museum (Museo Egizio di Torino) in Italy, shows the huts of the Egyptian miners, the road to the gold mines and the hills within which the gold veins occurred. The map is 0.4 × 2.8 m; it is believed that it was made during the reign of Ramses IV (1162–1156 BC). The scroll was found in a tomb near Thebes shortly before 1824 when it appeared in Turin. Ruins of these huts can be seen today at Fawakhir in the Eastern Desert.

In the old Egyptian language, the word *nubia* signifies a *gold field*. By 1300 BC, underground mining of vein gold was well established in Nubia under Egyptian control. There were over a 100 mines in the area. A series of forts were built to protect the flow of Nubian gold along the rich trade routes. Egypt became the dominant power in the Middle East, having the greatest gold-filled treasury in the ancient world.

The ancient Egyptians did not have an important port on the Mediterranean and all their trade was through the Red Sea. Coptos was at the starting point of the two great routes leading to the coast of the Red Sea, one toward the port of Tââ ou (Myos Hormos) and the other more southerly, toward the port of Shashirit (Berenice). Under the Pharaohs, the whole trade of southern Egypt with the Red Sea passed over these two roads. Under the Ptolemys,

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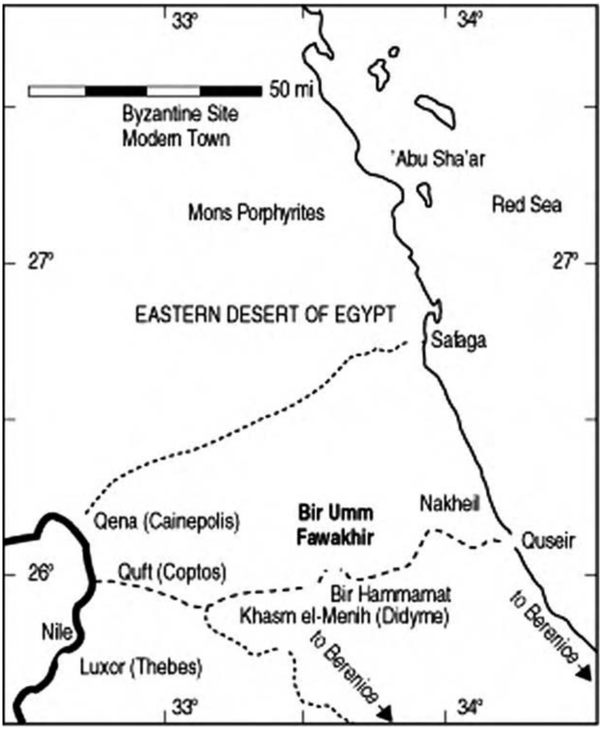

Fig. 1. Location of Coptos in Upper Egypt, the most ancient gold mining center.

and in Roman and Byzantine times, merchants followed the same roads for purposes of barter with the coasts of Zanzibar, Southern Arabia, India, and the Far East. This place and the surrounding area was known for the richness of its gold mines and semi-precious stones. A temple was built there by Tahutmes III, who ruled from 1503 to 1450 BC and was co-regent with Queen Hatshepsut for 21 years. The area that it occupied was about twice as large as his temple at Madinet Habu in Luxor. The Egyptians were the first to quarry gold-bearing rocks. This is well documented on wall paintings, an example of which is given in Fig. 2.

2. EARLY GOLD-MINING CENTERS

Herodotus (484–425 BC) refers to several great gold-mining centers in Asia Minor, and Strabo (63 BC) mentions gold mining in many different places. Pliny (23–79 AD) gives many details of ancient placer mining, which was extensive. The Romans had little of the metal in their own regions, but their military expeditions brought them major amounts in the form of booty. They

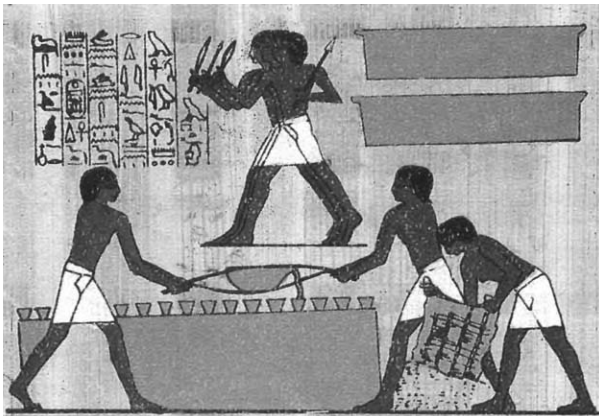

Fig. 2. Ancient Egyptian wall painting dating from about 1450 BC in the tomb of Rekhmire, vizier to Thothmes III at Thebes, showing metal workers casting molten gold in the moulds.

also exploited the mineral wealth of the countries they had conquered, especially Spain, where up to 40,000 slaves were employed in mining. The state's accumulation of gold bars and coins was immense, but during the barbarian invasions and the collapse of the empire this gold was scattered, and gold mining languished in the Middle Ages.

Following the discovery of America at the end of the fifteenth century, the Spaniards transferred considerable amounts of gold from the New World to Europe. Although the conquistadors found a highly developed mining industry in Central America, their efforts to increase gold production were largely unsuccessful because most of the finds consisted of silver. It was not until the discovery of deposits in Brazil, in 1691, that there was a noticeable increase in world gold production. Since about 1750 gold has been mined on a major scale on the eastern slopes of the Ural mountains. In 1840, alluvial gold was discovered in Siberia then at Coloma, California in January 1848, a few days before the signing of a treaty between Mexico and the United States to end their hostilities. California was thus ceded by Mexico after a discovery that was apparently not known to either government. Coloma is about 50 km southeast of Sacramento on the slopes of the Sierra Nevada. The discovery of gold in British Columbia was an epoch-making event. In the late 1850s, alluvial gold was found along the Thompson River, and in 1858 the famous Fraser River rush took place. Extraordinarily rich deposits were discovered in 1860 on Williams and Lightning creeks. For many years, British Columbia was the leading gold producer among the Canadian provinces and territories, but with the discovery of the Kirkland lake deposits in 1911, and the opening up of the Porcupine district in 1912, Ontario held first place ever since.

Gold deposits were also found in Eastern Australia (1851), Nevada (1859), Colorado (1875), Alaska (1886), New Zealand and Western Australia (1892), and Western Canada (1896). However, these deposits soon lost much of their importance. The strongest impetus was given to gold production through the discovery of the goldfields of the Witwatersrand in South Africa in 1885. South African gold soon occupied a commanding position in the world market. Production grew continuously except for a short interruption by the Boer War (1899–1902). Gold mining in Ghana (Gold Coast) began to play a modest role in the twentieth century, although the deposits were known in the Middle Ages.

3. GOLD AND ALCHEMY

To the medieval alchemists gold has been regarded as a metal of perfection. They identified it with the sun by virtue of its bright yellow color and it was given the symbol of a circle with a dot in the center. Gold was so precious that from earliest times man has left no stone unturned in searching for it in nature. It is not surprising, therefore, that humans should have sought to convert other metals into gold. The agent for transmuting base metals into gold was known as the *philosopher's stone*. In addition to its transmutatory power, the stone was believed to have the properties of a universal medicine for longevity and immortality. The attempts to transmute base metals into gold and to prolong life indefinitely, contributed much to modern chemistry in the form of new chemical substances and laboratory techniques. Alchemical principles have also found their way into modern psychological ideas, notably by the Swiss psychiatrist Carl Jung (1875–1961).

Ancient Egypt is considered the birthplace of alchemy. Zosimos (*ca.* 350–420), who taught in Alexandria, is the earliest writer known to have practiced alchemy. Because of their lack of knowledge of the composition of common substances some alchemists viewed many ordinary chemical reactions as transmutations. For example, the deposition of copper on iron metal placed in a solution of blue vitriol (copper sulfate), a reaction known since Roman times, was assumed by some to be a transmutation of iron into copper until the late Renaissance. Similarly, the mineral galena [PbS], on heating, liberates sulfur dioxide and appears to be transformed into silver, which is often present as an impurity in galena.

Through the centuries gold-making has been alternately encouraged and banned by monarchs and the Church. For example, Diocletian (AD 245–316), Emperor of Rome from 284 to 313, fearing that the Egyptians (Egypt was then under the domination of the Roman Empire) might become powerful through their knowledge of alchemy ordered in AD 296 all books and manuscripts "which treated the art of making gold and silver" to be burned. Consequently, only very few Egyptian alchemical works have been preserved. During medieval times European kings and princes supported alchemists at their courts hoping to acquire wealth through their work.

4. USES OF GOLD

Man valued gold for its lustrous color and its resistance to tarnishing and so it was used for special decorative ornaments and jewellery. The veneration reserved for gold by the ancients has led to its use for many centuries for religious artefacts. Gold was often cast in form of idols or hammered into foil to make masks for the dead. Gold was employed for barter and subsequently for coinage. By the eighth century BC small irregular bars of impure gold were being exchanged as currency in Asia Minor and by the fifth century BC gold coins were being used freely. Even today the majority of the gold produced is turned into gold bars, *i.e.* bullion that acts as the standard for the world's monetary systems, and they are used in international trade and exchange.

Gold differs from most other metals in that the majority of the metal that has ever been mined is still in existence. The total amount of gold now in existence is estimated to amount to around 125,000 t. If all of this gold could be collected together it would produce a cube with an edge of about 18.6 m. Gold has always been a symbol of immortality, and this was also a common subject in mythology. For example, King Midas requested that everything that he touched be turned into gold. When this blessing had turned out to be a curse in disguise, Midas prayed to Bacchus to take back his gift. The myth of the Golden Fleece has been subject to various interpretations. The legend of El Dorado, the Indian ruler who plastered his body with gold dust in festivals, led to the rapid conquest of South America. In an ancient Sanskrit text, there is a reference to *Pipilika* gold (the Sanskrit word for *ants*), which refers to gold particles that are collected by ants and then presented to the king in a special ceremony. In *Thousand and One Nights*, there are numerous references to palaces being built using bricks made of gold.

Gold ornaments have been found in Egyptian tombs of the prehistoric Stone Age, and the Egyptian goldsmiths of the earliest dynasties were skilful artisans. Today, gold used in jewellery is about 2,000 t annually worldwide, which represents 75% of the total consumption. Gold in jewellery serves different purposes in different parts of the world. In the West, it has a primarily decorative role; it is not normally regarded as an investment and consequently the gold used for this purpose is less pure. In the East, exactly the reverse is true; gold has a strongly monetary role there, is typically high caratage (22 carat – 91.7% pure gold, or 24 carat – 100% gold) and is bought and stored as an investment. It is typically worn by women and so has an ornamental role as well; the presence of large amounts of gold ornaments in oriental bazaars attests to this fact. The American Indians before the Spanish conquest used gold for ornaments but also as offerings in religious ceremonies, or to be buried with the deceased.

The extreme ductility of the metal is shown by the fact that 1 g can be pulled into a wire 3 km long. The gold threads that were used in embroidery and weaving were made in a variety of ways. Generally speaking, they consisted of metal strips that were used either directly or, more often, in the production of composite threads, in which the metal strip was wound around a fibrous core of silk, linen, cotton, or other yarns. Wire was also used directly or for winding around such cores.

4.1. Gilding

Because of its occurrence in nature in minute amounts, gold was an expensive metal. It was not necessary to have articles made of solid gold since it was possible to prepare gold in thin foils and cover the object completely with them so that they appear as if they were made of gold. Gilding is the art of applying and permanently attaching gold leaf or gold dust to surfaces of wood, stone, and metals. Gold is the most malleable of metals, and can be reduced to extremely thin leaves by hammering. Such leaves sometimes do not exceed 0.1 μm (1,000 Å) in thickness, and transmit green light. One gram of gold can be made to cover nearly 1 m^2 of surface. Many objects gilded by the Egyptians have survived to this day and the treasure of Tutankhamen's tomb is one example of their skill (Fig. 3). The Egyptians appear to have been the earliest practitioners of the art of making thin gold foil and the illustrations on tombs at Saqqara and Thebes show their goldbeaters working together with gold founders and goldsmiths (Fig. 4).

Gold foil was first used for gilding and when the technology was developed, the foil became thinner and thinner and was referred to as gold leaf. The invention of gold leaf was impossible before the perfection of methods for the purification of gold, as only pure gold or gold-rich alloys free from certain impurities can be beaten out to produce the thinnest leaf. Indeed, the methods of beating gold have not changed significantly since the days of the early Egyptians. The rounded stone has been replaced by a cast iron hammer with a wooden shaft and some machinery has been introduced to reduce the effort of beating by hand but, in essence, the process remains the same. The ability to make gold in very thin leaves made it more economical to use for gilding large objects such as statues, ceilings, columns, domes of churches, *etc*, with the minimum consumption of gold. Gold leaf is insufficiently strong to support its own mass and so new methods of attaching it to the substrate had to

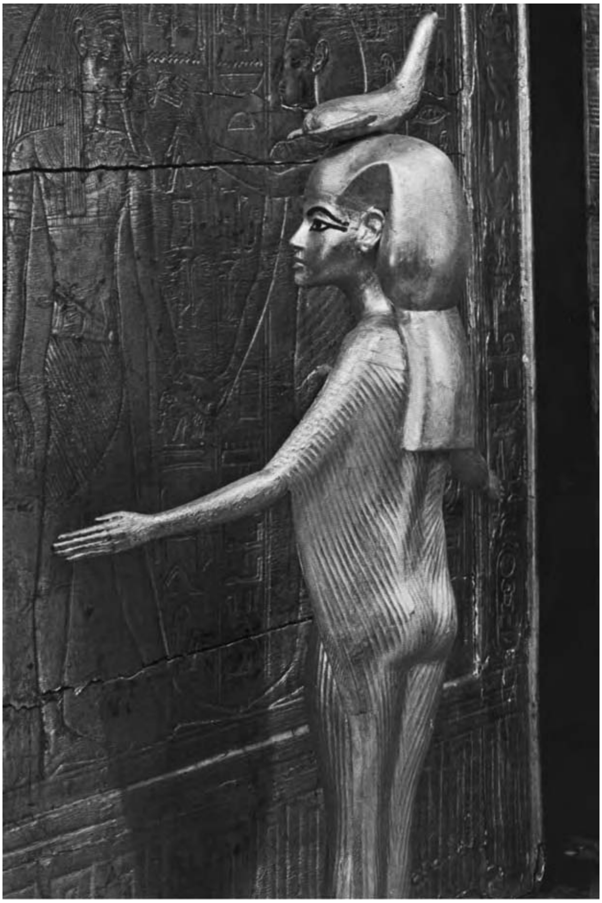

Fig. 3. Thin gold foil covering a wooden statue from an ancient Egyptian tomb.

Fig. 4. An ancient Egyptian wall painting showing a worker preparing gold foils.

be developed. One obvious way was to use an adhesive and this method is still used today for the gilding of wood and stone and for the decoration of leather book-binding.

4.1.1. Gilding of metals

When the gold leaf is applied on metal, the adhesion of the gold is enhanced by the application of heat to promote inter-diffusion with the underlying metal. To cover a large metallic object such as the dome of a church or a statue standing in the street with a very thin layer of gold that would resist exposure to rain and wind, mercury use was made of as a sticking medium. Copper and not bronze or brass was usually the metal of choice, although it is more difficult to cast than the alloys. The reason is that the alloying elements tin, zinc, and lead interfere with the gilding process because these metals have a high solubility in mercury and thus result in a defective layer. Although gilding with mercury was a rare and costly process in the first century AD it had become the standard method of gilding by the third or fourth centuries and it remained unchallenged throughout history.

Two processes were developed to gild a copper substrate. In the cold process, mercury is rubbed on the clean copper surface until it has a mirror-like finish. Some copper dissolves in the mercury and forms a thin layer of copper amalgam. Any excess mercury is mechanically removed. Gold leaf is then pressed upon the surface. It bonds with the copper-amalgam very firmly. More than one layer of gold leaf is usually necessary to obtain the desired color. The hot process was developed at a later date to gild copper alloys and overcome the difficulty of casting unalloyed copper. In this method gold leaf is dissolved in mercury; this takes place very rapidly. The amalgam is applied on the copper substrate to the desired thickness. The object is then heated to expel the mercury, leaving a tenacious gold layer. The poisonous fumes emitted during the process were a health hazard not only to the workers but also to those living in the neighborhood of a gilding workshop. St. Isaac's cathedral in St. Petersburg was constructed in the 40-year period 1818–1858 with a gilded dome 21.83 m in diameter.

4.1.2. Gilding of glass and porcelain

The gilding of glass, porcelain, and pottery, ranging from the simple edging on a plate to the elaborately decorated vase with richly gilt panels, has always been a prominent feature in industry. The Chinese applied gold leaf over a layer of linseed oil and litharge [PbO], or with egg white or shellac; however, these gilded layers were not durable. Other workers used gold leaf ground up in honey, washed, dried, and applied with a flux; in these cases; however, the product was expensive because the gold layer was thick. The German chemist Johann Kunckel (1630–1703) discovered the precipitation of gold powder by the addition of a solution of ferrous sulfate to a solution of gold in aqua regia. This was published in his book *Laboratoria Chymica*, which appeared in 1716, thirteen years after his death. The precipitate, separated by decantation and then dried, was thoroughly mixed with a finely ground lead-silicate flux and applied to the ware, then fixed by heating in a kiln. In 1827, a new gilding process was discovered in the Meissen factory near Leipzig by Heinrich Kühn. The process consisted of a solution of gold chloride in *balsam of sulfur*, an oily substance obtained by reacting sulfur with turpentine. This medium, which is of somewhat unknown chemical composition, had been known for many years. Kühn was thus able to produce a liquid preparation of an organo-gold compound that, on firing at a relatively low temperature, yielded a bright and shining gold that needed no polishing.

4.2. Gold in the glass industry

In the 1650s, the German chemist Andreas Cassius (1605–1673) discovered a purple pigment that can be used in coloring glass and porcelain, yielding an exceptionally beautiful purple color. The color was known as *Purple of Cassius*. It was prepared by adding a solution of stannous chloride to a dilute gold chloride solution and was applied in the most famous glass and porcelain factories of Europe in Meissen and Sèvre. The nature and constitution of *Purple of Cassius* presented scientists with a problem that was tackled throughout the whole of the nineteenth century by some of the most distinguished chemists of the time. Not until the turn of the century was the true nature of this pigment elucidated. Richard Zsigmondy (1865–1929), a Viennese chemist who had spent some years studying gold colors and had joined the Schott Glassworks in Jena in 1897, developed the ultramicroscope for the examination of colloids. He showed conclusively that the *Purple of Cassius* consisted of very finely divided gold with stannic oxide. For this investigation, he was awarded the Nobel Prize in Chemistry in 1925.

In modern times gold films deposited on glass by thermal evaporation are superior to other metals for reflectivity in the infrared wavelength range. Such films applied to glass windows for offices permit good vision by substantially reducing the transmission of infrared energy by reflection rather than by absorption. The cost of production is very low and the economy in energy saving due to cutting down on heating in winter or air conditioning in summer is appreciable. Many modern office buildings are now constructed using glass windows with a gold coating about 0.01 μm thick. In the deposition process, gold is heated to about 1390°C and at a low pressure. This creates a vapor pressure of gold and $2 \times 10^{-4}\,\mathrm{g\,cm^{-2}\,s^{-1}}$ will evaporate. The vaporized gold atoms move in nearly straight lines from the source to the surface to be coated.

5. OCCURRENCE OF GOLD

Most gold occurs as native metal, nearly all alloyed with various amounts of silver as the mineral electrum, but not with copper. Certain minerals are characteristically associated with gold, and the most important are pyrite [FeS_2], galena [PbS], zincblende [ZnS], arsenopyrite [FeAsS], stibnite [Sb_2S_3], pyrrhotite [$Fe_{(1-x)}S$], and chalcopyrite [$CuFeS_2$]. Various selenium minerals and magnetite [Fe_3O_4] may also be present. In Witwatersrand, South Africa, uraninite [UO_2], and to a lesser extent, thucholite [a variable mixture of hydrocarbons, uraninite and sulfides] are associated with the gold ore; uranium was recovered as a by-product of gold milling. Carbonaceous matter is associated with some gold ores. Gold has affinity for tellurium and it forms two main telluride minerals: calaverite [$AuTe_2$], and sylvanite [$(Au,Au)Te_2$]. It was in these minerals that tellurium was first discovered. On the other hand, it occurs with palladium as porpezite (Au containing 5–10% Pd), and with rhodium as resinrhodite [Au, Rh]. In placer deposits, it may be present as minute particles or large nuggets. In certain ores known as *refractory* ores, gold is associated with sulfide minerals in an extremely finely divided state.

Ouro Preto, or black gold, is the name of an old town in Brazil about 400 km north of Rio de Janeiro. It was near there that gold was first discovered in Brazil in 1691 and resulted in the Brazilian gold rush. The Brazilian gold was black in color, hence the name *ouro preto*. In these deposits, gold occurred as fine particles covered with a thin black coating. In 1876, the Brazilian emperor Dom Pedro II (1825–1891) inaugurated the first School of Mines in Brazil in Ouro Preto.

6. PROCESSING OF GOLD ORES

6.1. Gold panning

Gold played a central role in the development of metallurgy. At one time, however, there was no need for any chemical or metallurgical knowledge to recover gold; it occurred in nature in the native state and simple panning was enough to collect the glittering particles and sometimes nuggets. Because gold has such a high density (19.3 g/cm^3), panning can be used to easily separate it from the sand and gravel with which it is associated. In this method the material is mixed with water in a shallow pan and by careful swirling the impurities can be washed away, leaving the gold behind. However, this requires great patience and hard work. Gold collected by panning or from rich veins was melted to recover it as relatively pure metal. With earlier primitive methods, only the easily accessible, pure gold was obtained. As machinery was developed and extraction processes perfected, mining was extended to less rich deposits. For low-grade deposits, other methods were developed.

6.2. Amalgamation

Although mercury was known to the ancient Chinese and Hindus, and has been found in Egyptian tombs dating back to 1600 BC, it was extracted and used only in the Roman times. Mercury ores occur in abundance in Italy and Spain. The Roman writer, Dioscorides mentioned its preparation from cinnabar. Pliny gave a method of purifying mercury by squeezing it through leather. He described the amalgamation process and introduced the term *amalgam*, from *malagma* (meaning *I soften*, because mercury softens gold). An alchemical representation of the amalgamation of gold is shown in Fig. 5.

Although the Romans were acquainted with the fact that mercury dissolves gold and silver, it does not appear that they applied this knowledge to the extraction of these metals from their ores. Vanoccio Biringuccio mentioned the amalgamation of ores in his book, *De la Pirotechnia*, published in 1540, as does Georgius Agricola in his book *De Re Metallica*, published in 1556. Mercury dissolves gold rapidly at ambient temperatures; an amalgam containing 10% gold is liquid, that containing 12.5% gold is pasty, and that containing 15% gold is solid.

Stamp mills (see Fig. 6) were closely associated with the amalgamation process. A stamp mill is a grinding machine where the grinding action takes place by falling weights. The ore from the crushers varying in size from 10–60 mm is fed with water in the stamp mill. A *stamp* is a heavy iron pestle 3–5 m long and about 7 cm in diameter carrying a weight 200–400 kg. The stamp is raised by a cam that is keyed on to a horizontal revolving shaft and

Fig. 5. Alchemical representation of the amalgamation of gold: mercury conquers gold, the king of metals.

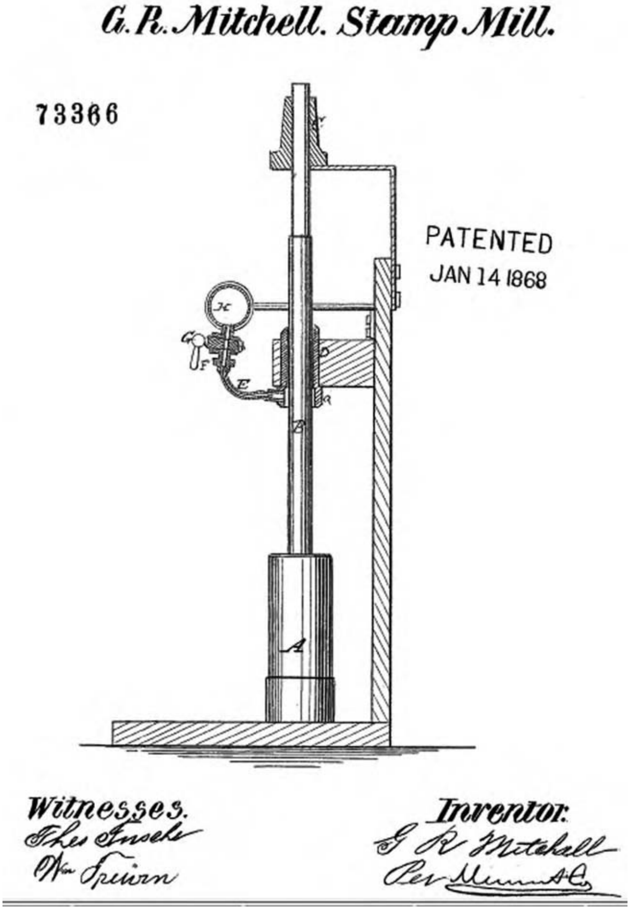

Fig. 6. Stamp mill dated 1868 used for crushing gold ores prior to amalgamation.

allowed to fall by its own weight. Mortars are made of cast iron about 1.2 m long, 1.2 m high and 0.3 m wide. The height of the drop of the stamp varies between 30 and 50 cm and the number of drops per minute varies from 30 to 100. Five stamps are usually present in one mortar.

Fine powdered ore slurry containing native gold and silver is then passed over copper plates amalgamated with a thin layer of mercury onto which the noble metals adhere. Depending on the gold content of the ore, the amalgam is scraped once or twice a day and a fresh mercury surface is exposed. About 3–10 t of ore per square metre of mercury surface are usually employed, *i.e.* a mercury consumption of about 30–50 g/t ore. The amalgam is washed with water to remove any attached gangue particles, then pressed to remove excess mercury. An amalgam containing 40–50% gold can be obtained. It is charged on trays and heated in a horizontal retort to distil the mercury. A gold sponge is obtained, which is then melted with fluxes then cast as a bullion. Gold bullion contains some silver, copper and other metals, which are separated at mints or private refineries.

The amalgamation process was used extensively for the recovery of gold and silver from their ores. In many countries it is now illegal to use this process because of the toxicity of mercury. In spite of this, the process is used on a large scale by numerous small illegal operators in several parts of Africa and by the so-called *garimpos* in the Amazon basin in Brazil. This practice has resulted in the mercury pollution of soil, rivers and also the atmosphere because the final step of gold recovery is usually done by heating with an oxygen flame in the open air to remove the mercury, a hazardous procedure.

6.3. Chlorination

Gold, the most noble of all metals, was insoluble in all acids and alkalis known at that time. The discovery of *aqua regia* by the Arab alchemist Jabir Ibn Hayyan (720–813 AD) and its ability to dissolve gold introduced a new technology for the extraction of gold from its ores. *Aqua regia* or *royal water* (the water that dissolves the king of metals) is a mixture of hydrochloric and nitric acids, neither of which alone can attack gold! An alchemical symbolization of this process is shown in Fig. 7. In modern terms the action of the mixture is due to chlorine and nitrosyl chloride.

Chlorine was discovered and isolated by the Swedish chemist Carl Wilhelm Scheele (1742–1786) by the action of hydrochloric acid on manganese dioxide in 1774; Scheele also noted that it attacked all known metals. This knowledge was first applied to the recovery of gold from its ores in 1851 by Karl Friedrich Plattner (1800–1858) of Freiberg using aqueous solutions of the gas. Although the concept of the transmutation of metals was abandoned by the chemists of the nineteenth century, metallic iron was used to displace gold from the chloride leach solution. A variation of this technology was the barrel chlorination process, in which chlorine gas was generated by means of bleaching powder and sulfuric acid inside a rotating barrel. In 1863, Plattner's method of chlorination was introduced in gold mines in the United States and shortly afterwards in Australia.

6.4. Cyanidation

The cyanide process was based on the fact that dilute cyanide solutions will dissolve gold from its ores and that when the solution is brought into contact with zinc, gold will be precipitated. The cyanide process has been a great help in the extraction of gold at the Witwatersrand deposit because gold occurred in such fine particles that extraction of only 55–65% could be obtained by amalgamation and chlorination. Today about one billion tons of ore are treated

Fig. 7. Alchemical depiction of *aqua regia* – the lion eating the sun (gold).

annually world wide using cyanide solution to recover gold, representing the largest tonnage of any mineral raw material that is treated chemically.

To understand the factors that led to the discovery of the cyanidation process, it is essential to refer to the activities of chemists during the eighteenth century. Extensive researches were under way in the emerging chemistry of the so-called *Blue Acid* and its compounds. Chemists at that time were occupied with a number of blue-colored compounds obtained by heating dried blood with potash [K_2CO_3] and then treating the aqueous extract with iron vitriol [$FeSO_4$]. The precipitate obtained thereby yielded an intense blue pigment. Its accidental discovery was made in Berlin in 1704, by the German alchemist Johann Conrad Dippel (1673–1734) and therefore the pigment became known as *Berlin blue*. In English literature, it became known as *Prussian blue* to refer to Prussia, the former state of northern Germany. This new blue pigment immediately displaced the naturally occurring ultramarine blue pigment because it was much cheaper. It was the first artificially manufactured pigment and its discovery opened up a new field of chemistry, the chemistry of cyanogen compounds.

The French chemist Pierre Joseph Macquer (1718–1784) discovered in 1752 that when Berlin blue was boiled with alkali, iron oxide separated out and the remaining solution when concentrated by evaporation yielded yellow crystals, now known as potassium ferrocyanide. In 1782, Scheele heated the blue pigment with dilute sulfuric acid and obtained an inflammable gas that dissolved in water and reacted acidic with litmus paper; he called it *Berlin blue acid* or simply the *blue acid* (*blausäure*), which was also used in Germany during World War II in gas chambers. In 1811, the French chemist Joseph Louis Gay-Lussac (1778–1850) liquified the gas (boiling point 26°C) and determined that its composition was HCN. When Berlin blue was heated with nitric acid, a red/violet compound was obtained, which became known as *prussiate* in reference to Prussia. In 1822, Leopold Gmelin (1788–1853) in Germany prepared potassium ferricyanide in the form of deep red prisms, by passing chlorine into a solution of potassium ferrocyanide.

As we know today, blood contains the red pigment *hemin*, which is an iron chelate containing a porphyrin structure. The building units of this structure are alkylated pyrrol nuclei. On heating with potash, potassium ferrocyanide is formed; this is extracted by water and reacted with iron salt to form ferri-ferrocyanide. When numerous new compounds of the blue acid became known, Greek terminology was introduced to name them. *Kyanos* in Greek means *blue*; hence, the modern term cyanide was used for compounds derived from the blue acid. Potassium ferrocyanide became a commercial product around 1825. Production of potassium cyanide followed a few years later. The dissolving action of cyanide solution on metallic gold was known as early as 1783 by Scheele, who experimented with the hydrogen cyanide gas he discovered. The solution obtained by dissolving gold in cyanide solution was used by George Elkington (1801–1865) and his Cousin Henry Elkington (1810–1852) in England in 1836 to prepare the bath necessary for electroplating gold.

In 1835, the formation of HCN in blast furnaces became known, and in 1843, the existence of cyanogen compounds in coal gas was discovered (in the 1950s, cyanides were also identified in different forms and at different locations throughout a petrochemical complex). Coal gas was produced in large amounts for heating and illuminating purposes; it was the equivalent of today's electricity. Because of their poisoning action, it was necessary to remove cyanogens; this was accomplished by absorption, using a mixture of ferrous and ferric hydroxides. Many other processes were developed that contributed considerably to an understanding of the chemistry of cyanides, cyanogens, thiocyanates, cyanates, cyanamides, amides, nitrites, guanidines, and other related compounds.

The dissolution reaction was studied by noted chemists of the time, *e.g.* Prince Bagration in Russia (1844), Franz Elsner in Germany (1846), and Micheal Faraday in England (1857). It remained, however, for John Stewart

MacArthur (1856–1920) in Glasgow in 1887 to apply this knowledge to gold ores. When the process was applied industrially, research was initiated in many universities. The most important was that by the German chemist Guido Bodländer (1855–1904) at the University of Breslau (now Wroclaw in Poland) in 1896, whose contribution was twofold: he confirmed that oxygen was necessary for the dissolution as claimed by Elsner and Faraday and doubted by MacArthur and he discovered that hydrogen peroxide was formed as an intermediate product during the dissolution of gold. The action of cyanide solution on gold remained a mystery for a long time for three reasons:

- It was difficult to understand why gold, the most noble of all metals, which could not be attacked by any strong acid except hot concentrated *aqua regia*, could be dissolved at room temperature by a very dilute solution (0.01–0.1%) of NaCN or KCN.
- A strong solution of NaCN was found to be no better than a dilute solution, whereas in the case of other metals dissolving in an acid, for example, the more concentrated the acid, the faster the metal dissolved.
- It was not obvious why oxygen was necessary even though, alone, it has no action whatsoever on gold.

The mystery was resolved about 60 years after the discovery of the process when it was realized that the dissolution of gold in cyanide solution is an electrochemical process, *i.e.* similar to a galvanic cell. This has been demonstrated by embedding a small gold sphere in a KCN gel to which air was introduced from one direction. It was found that the gold corroded at the surface far away from the air flow, *i.e.* an oxygen concentration cell was formed around the sphere; the surface less exposed to oxygen acted as anode while the surface in direct contact with oxygen acted as cathode. Thus, oxygen picks up electrons from the gold surface while gold ions enter the solution and are rapidly complexed by the cyanide ions.

By analogy with the ‘transmutation’ of iron into copper, MacArthur used zinc shavings to precipitate gold from the cyanide solution. The process became more efficient when zinc dust was introduced by Charles W. Merrill (1869–1956) in 1904 and further improved when Thomas B. Crowe removed air from the solution by passing it through a vacuum tank before introducing the zinc. This new technique, developed in the USA, later became known as the Merrill–Crowe process.

Activated charcoal was first applied in metallurgy for the recovery of gold by the chlorination process. When this process was displaced by cyanidation, charcoal was also used for the new process because large stockpiles of activated charcoal from gas masks were available after World War I when poisonous gas was used in combat and the charcoal in the masks no longer needed. In both cases gold was recovered from the gold-laden carbon by burning the carbon to ashes and melting to bullion, which was a wasteful process. This disadvantage, coupled with the major advances that were made in the technology of gold recovery by precipitation with zinc dust at that time, led to abandoning the process utilizing activated carbon. In the early 1950s, however, interest in the metallurgical application of activated carbon was revived when a procedure was developed by Jack B. Zadra at US Bureau of Mines for the elution and electrowinning of gold and silver adsorbed on carbon granules, which allowed re-use of the carbon, and the utilization of the process as a concentration purification step. Practical developments in the 1980s led to a widespread application of the carbon-in-pulp technology. The adsorption capacity of activated carbon for metal ions is small compared with that of ion exchange resins; however, activated carbon is a much cheaper material to manufacture and is more selective. The process also has the advantage of eliminating an expensive filtration operation.

6.5. Refining of gold

There are three methods for the refining of gold. The hydrometallurgical process is the oldest and depends on the gold content and the type of impurities present. While silver is soluble in both nitric and sulfuric acids and gold is insoluble, these acids cannot be used to dissolve silver away from an alloy containing more than 25% Au. For high-gold alloys, *aqua regia* is therefore used. In such alloys, gold is leached, while silver forms an insoluble residue. Further, gold is soluble in *aqua regia*, but a gold–silver alloy containing more than 85% Ag cannot be attacked due to the formation of an insoluble layer of AgCl, which stops the attack. Therefore, the *aqua regia* leaching process is used only for refining high-gold bullions, where the silver content does not amount to more than 8%, or to cases where the bullion contains enough copper to open it up to attack in spite of the silver present.

The chlorination process was first applied at the Sydney Mint in Australia in 1867 by F. B. Miller. It is based on the fact that chlorine readily combines with silver and the base metals present, forming chlorides, before it starts to attack gold.

The electrolytic process was invented by Emil Wohlwill in 1874 at the Norddeusche Affinerie in Hamburg.

6.6. Some recent trends in gold ore processing

The cyanidation process has remained practically unchanged since its discovery, but tremendous engineering developments have occurred, making it very efficient. The developments include the introduction of heap leaching, the application to the so-called refractory ores, the improved use of activated carbon technology, and the increased attention paid to the abatement of pollution. The increased price of gold in the 1970s made possible the leaching of old tailings containing as little as 1 g/t gold thanks in part to the newly developed heap-leaching technology that was developed for the leaching of low-grade copper and uranium ores, with agglomeration where necessary.

Refractory ores were often treated by roasting followed by leaching, but this could be an expensive proposition, as well as creating potential environmental issues. A hydrometallurgical approach proved to be a successful solution for this type of ores, for example that now in operation at Goldstrike, using horizontal autoclaves operating at 160–180°C and 2,000 kPa. Gold ores containing carbonaceous material are also known as refractory ores and are difficult to treat, not only because part of the gold is tied up with the organic matter but also because dissolved gold is adsorbed on the carbon present in the ore and therefore reports in the tailings. This problem was solved by aqueous oxidation using chlorine. Some of the gold may be solubilized by the chlorine water but the major function of the controlled chlorination is to oxidize organic matter before cyanidation. A plant at Carlin, Nevada, used this technology. Another solution to this problem was found by using the carbon-in-leach process as described below.

Cyanidation under high oxygen pressure has recently been used commercially at the Consolidated Murchison Mine near Gravellote in South Africa. The process has been developed by Lurgi in Germany using tube autoclaves 1.5 km long and 5 cm inner diameter. Leaching is conducted at ambient temperature but at about 5 MPa oxygen pressure. As a result, residence time is only 15 min at 85% recovery. It should be noted that at high oxygen pressure, a high cyanide concentration must be used to achieve high reaction rates. In practice, the leach solution is 0.2–0.5% NaCN. Although cyanide solutions are susceptible to oxidation, the short residence time renders this drawback negligible.

The carbon-in-leach process is another variation that was developed to circumvent problems faced when leaching gold ores containing carbonaceous material, *i.e.* low recovery because of the adsorption of the gold cyanide complex on the organic matter, which then reports to the tailings. In this process the carbon granules are added during leaching of the ore so that any gold dissolved, is immediately retained by the carbon and not by the carbonaceous matter in the ore.

7. GOLD STANDARDS AND ASSAYING

Gold is too soft in the pure state for the purposes to which it is generally applied. For practical application it is alloyed with copper or silver. The former renders the gold more red and the latter metals paler than their true colors. The proportion of gold contained in an alloy is expressed in *degrees of* *fineness* or as *carats. Fineness* is expressed in parts per thousand, for example 916.6, or decimally 0.9166. The carat is expressed in parts of 24, pure gold being 24 carats fine. Thus 9-carat gold contains 9 parts of pure gold and 15 of some alloy of copper and silver. For several thousand years, weighing seems to have been restricted to determining the mass of gold.

Georgius Agricola (1490–1555) described the use of the touchstone and touch needles for examining bullion, coins, and jewellery. *Touching* involves rubbing the alloy under investigation onto the surface of a piece of smooth, fine-grained, slightly abrasive black stone and comparing the color of the streak produced with those obtained from standard alloys. The method was already known to the ancient people. Theophrastos (371–288 BC) gave a detailed description of touchstone in his book on stones. The touchstone method of assay was also discussed in Sanskrit texts (third century BC) describing the manufacture of touch needles (standard alloys) in which the ratio of gold to copper is varied in steps. By the Renaissance, the sets of touch needles had grown to include ternary alloys of gold, silver, and copper.

The gold content of ores and rocks is commonly determined by means of a *fire assay*, a method known to metalworkers for 3,000 years. A weighed sample of pulverized rock is melted in a mixture of flour, lead oxide, soda, borax, and silica within a furnace at temperatures that range from 900–1,000°C. The lead oxide is reduced easily to the metal, which collects the gold, and this lead–gold melt separates to cool as a button. The button is then re-melted in a bone-ash cupel, which absorbs the lead oxide formed but leaves behind a bead of gold that is weighed to obtain the ratio of gold to rock. The basic unit of weight used in dealing with gold is the *troy ounce*, so named after Troyes, a town south of Paris on the Seine that is famous for its medieval fairs and where the pound of Troyes ($\sim$12 oz) was in use. One troy ounce is equivalent to 20 troy pennyweights. In the jewellery industry, the common unit of measure is the pennyweight (dwt), which is equivalent to 1.555 g. The *avoirdupois pound* was also developed in France and was based on 16 oz (*avoir-du-poid* in Old French, meaning *goods weight*).

Incidentally, gold has almost exactly the same density as tungsten, 19.3. In the 1970s, a person deposited gold-plated tungsten bricks in a bank in lieu of true gold. The fraud was discovered later, and since then all gold bullion deposits are now routinely examined by banks by neutron diffraction to confirm their identity.

8. GOLD IN CURRENCY

Gold has been used as a medium of exchange and as a form of savings from the earliest times to the present day. For many civilizations gold and money have been, and still are, regarded as one and the same thing. The East Slovak Museum in Košice has one of the largest collections of gold coins in the world, dating back to the eighteenth century. The collection, comprising 2,500 pieces, was discovered in a box buried under a building during construction. It is believed that the owner had to flee in a hurry during a revolution.

The first use of gold coins is attributed to the Chinese. In the West, the first gold coins were minted by the Lydians in Asia Minor from around the sixth century BC. It was only in the fifth century BC, however, that techniques were developed to produce pure gold coins by removing the naturally occurring silver content. Thereafter, coins became more important and were widely produced by the Romans in a variety of metals, besides gold. Metals other than gold were commonly used for coinage for much of history. The scarcity of gold precluded its widespread use as a means of payment. It was only with the major gold discoveries of the nineteenth century that gold became widely used as a form of currency.

9. BANKS

There is a close historical relationship between the growth of banks and the use of gold as money. At one time, people would leave their gold at goldsmiths, who had safe places to store the gold. Carrying gold around as a means of exchange was inconvenient because of its weight and great value. To facilitate trade, goldsmiths began to issue certificates of deposits of gold, which were handed over as payment. These were equivalent to today's cheques.

The second step, which completed the transformation from being a goldsmith to being a bank, was the realization by goldsmiths that the majority of the gold sitting in their vaults was rarely withdrawn at the same time. This meant that the goldsmiths could lend out a portion of the gold in their vaults. They could charge interest for the loan and so make a return. If they lent gold prudently, they could still retain enough gold in their vaults to honor the daily demands for withdrawals from their depositors.

As a result of the goldsmith/bank's activity there was a net increase in the amount of money in circulation. In 1717, Sir Isaac Newton, then Master of the Mint in London, fixed the value of the British pound in terms of its value in gold, since the price of an ounce of gold was set at four pounds seventeen shillings and ten and a half pence. In the early nineteenth century, discoveries of gold in California and elsewhere greatly increased the world stocks of gold. For the first time, there was sufficient gold to act as the sole basis for monetary systems. Starting with the UK in 1816 and culminating with the USA in 1900, the majority of the world's trading nations adopted the gold standard. This meant that gold was minted into coins and circulated as currency. These coins were not token money, since they provided full value.

Because of gold's bulk, bank notes were issued in a number of countries. The gold backing to this paper currency meant that the notes could be taken to the bank at any time and cashed in for the prescribed amount of gold. During the financial crisis caused by World War I most countries suspended the convertibility of their currencies into gold. The warring nations decided to conserve their reserves to finance the war effort. They would otherwise have been in danger of losing their gold reserves as the gold standard moved to correct the balance of payments deficits they found it necessary to run.

After World War I bank notes were made legally acceptable at their face value, and the requirement for a complete gold covering for the money supply was removed. This gave governments the power to control the supply of money in circulation according to the needs of the economy. Gold did, however, retain its key functions as a measure of value and as a central bank reserve asset, although no longer exclusively but now in conjunction with foreign exchange. Consequently, currencies were still defined in terms of a specific amount of gold, but there was no obligation to deliver gold on demand and the value of money in terms of gold could be changed. This system was eventually ratified after World War II. Because currencies were still denominated in terms of gold there were still semi-fixed exchange rates between nations. The USA fixed its currency at $35 per ounce, although US citizens were banned from holding gold. As a result the dollar took on the role of the official monetary price of gold. Many countries began to denominate their currencies relative to the dollar, which came to be regarded as "as good as gold".

By the late 1960s, the US balance of payments had slipped so far into deficit that the dollar was perceived to be overvalued relative to gold. Many gold mines were shut down because the cost of production was higher than the value of gold recovered as fixed by the government. The USA revoked its undertaking to pay dollars in exchange for gold in August 1971. Eventually the gold price was left to find its own level. Consequently gold rose progressively through the 1970s, rising to its all time high of USD 850/oz on 21 January 1980.

A large part of the gold stocks of the United States is stored in the vault of the Fort Knox Bullion Depository located about 50 km south-east of Louisville in Kentucky. Gold in the Depository consists of bars about the size of ordinary building bricks (18 × 9.2 × 4.4 cm) that weigh about 12.5 kg each, stored without wrappings in the vault compartment.

Today gold is borrowed and lent in just the same way as money. Gold's interest rate is low in comparison with most currencies, which probably reflects the lower long-term risk of inflation in holding gold compared to currency. Interest rates vary within a range of 1–2%. Low interest rates make it attractive for companies in the gold business to finance themselves in gold rather than currency. From the mid-1980s mining companies wishing to raise money to develop new gold mines have commonly borrowed gold. The gold is then sold for cash to start development. When the time comes for repayment, the mine repays its debt in ounces of gold, from the new mine. So their financing is completely safeguarded against movements in the gold price, whereas if they had borrowed in dollars they would have been exposed to movements in the dollar price of gold. Gold has served the human race well as a dependable form of money from the earliest of times right up to the modern day.

10. GOLD MUSEUMS

The historical importance of gold to our civilization is attested by the number of museums devoted exclusively to this metal. There are four Gold Museums in South America and one in Central America preserving gold artifacts from Inca and other ancient civilizations. They are located in Bogota (Columbia), Lima (Peru), La Paz (Bolivia), Sabara (Brazil), and San José (Costa Rica). The Brazilian museum is located in the former palace of the Portuguese governor of the Province of Mina Gerais in a suburb of Belo Horizonte and shows the history of gold in Brazil.

A number of gold museums can be found in the other major gold-producing countries, for example, the Ballerat Gold Museum in Australia and the Gold of Africa museum in South Africa.

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Fathi Habashi, professor Emeritus of Extractive Metallurgy at Laval University in Quebec City. He was born in Minia, Egypt on October 9, 1928. He holds a B.Sc. degree in Chemical Engineering from the University of Cairo (1949), a Dr. Techn. degree in Inorganic Chemical Technology from the University of Technology in Vienna (1959), and honorary degrees from the Technical University of Oruro in Bolivia (1986) and the Saint Petersburg Mining Institute in Russia (1993). He held the Canadian Government Scholarship in Ottawa (1960–1962), taught at Montana College of Mineral Science & Technology (1964–1967), then worked at the Extractive Metallurgical Research Department of Anaconda Company in Tucson, Arizona before joining Laval in 1970. He was elected a Fellow of the Canadian Institute of Mining, Metallurgy, and Petroleum (1998) and holds its Silver Medal. His research interests are inspired by a desire to develop an integrated understanding of extractive metallurgical processes and to put them into a systematic order within a historical background. He was a guest professor at a number of universities and authored a number of books on extractive metallurgy.

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PART I PROJECT DEVELOPMENT

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Chapter 1

Sampling procedures

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1. INTRODUCTION

It is still surprising that sampling is often not given the attention it deserves and the task is delegated to personnel who do not fully appreciate the significance and importance of sampling. Yet correct sampling and sample processing practices are critical to accurate delineation of ore resources as well as the evaluation and control of subsequent processing operations from mining through to delivery of the final product (François-Bongarçon and Gy, 2002; Holmes, 2002, 2004). Cost is usually the driving force for this phenomenon, and this can result in major flaws in sampling procedures as well as selection of inappropriate sampling equipment. However, it is false economy, because there is no point in using the latest analytical methods and equipment and spending considerable time and effort estimating resources or attempting to reconcile production figures if the samples presented for analysis are not representative in the first place. If sampling is not carried out correctly, the entire measurement chain is corrupted at the outset and no amount of reanalysis will fix the problem.

2. SAMPLING BASICS

Samples are taken from a range of locations, including percussion and diamond drill holes, blast holes, relevant feed and product streams, trucks, trains and stockpiles. The fundamental rule for correct sampling and sample

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processing is that all parts of the material being sampled must have an equal probability of being collected and becoming part of the final sample for analysis (Gy, 1982a, b; Pitard, 1993), otherwise bias is easily introduced and the sample is not representative. Examples of poor sampling practices include loss of drill cuttings prior to sampling, taking a *grab* sample from percussion drill chips or the side of a stockpile, or taking a *dip* sample from a slurry tank. Percussion drill chips are bound to be segregated, so a grab sample will not be representative of all particle sizes. Similarly, coarse particles tend to rill down the side of stockpiles, so samples taken from the side of a stockpile will not be representative of all particle sizes and will not provide information on the material in the main body of the stockpile. Hence, such samples cannot possibly be representative of the whole stockpile; at best samples taken from the side of a stockpile may provide an indication of what was last stacked on the outside of the stockpile. In addition, segregation is typical of particles suspended in a slurry, with a greater proportion of the coarser and denser particles occurring near the bottom of the tank. Hence, it is impossible to take a representative sample of a slurry by taking a dip sample at a fixed depth using a ladle.

2.1. Importance of minimizing bias

The presence of bias is a major problem in sampling, because it does not average out over time. In contrast to poor precision, which can be improved by calculating the average of replicate sampling, sample preparation and analysis, no amount of replicate sampling and analysis will eliminate bias once it is present. The final result is just a more precisely incorrect analytical value. Consequently, minimizing or preferably eliminating biases is in many respects more important than improving precision. Sources of bias that can be eliminated at the outset by correct design of sampling and sample processing systems include sample spillage, sample contamination and incorrect extraction of increments, such as by taking a grab sample. Sources of bias that can be minimized but not completely eliminated include change in moisture content, size degradation and dust loss. Samples for determination of moisture content require special attention and must be extracted as quickly as possible with minimum handling and placed in impervious airtight containers or bags. They should then be returned to the laboratory without delay for weighing and moisture determination and not stored for long periods near the sampling point, particularly when the ambient temperature is high.

2.2. Overall precision

Once bias has been addressed, precision can be assessed by determining the overall variance of the final analysis (σ^2_{SPA}) by breaking up the sampling (and sample processing) variance into its components for each sampling stage, *i.e.*,

$1, 2, \ldots, i, \ldots, u-1$ (Gy, 1982a), as follows:

$$\sigma^2_{\mathrm{SPA}} = \sigma^2_{\mathrm{S}_1} + \cdots + \sigma^2_{\mathrm{S}_i} + \cdots + \sigma^2_{\mathrm{S}_{u-1}} + \sigma^2_{\mathrm{A}} \tag{1}$$

where $\sigma^2_{\mathrm{S}_1}$ is the sampling variance for Stage 1, $\sigma^2_{\mathrm{S}_i}$ the sampling variance for Stage i, $\sigma^2_{\mathrm{S}_{u-1}}$ the sampling variance for Stage $u-1$, the second last stage and σ^2_{A} the analysis variance, which includes selection of the final test portion.

This approach is particularly useful for designing, optimizing and assessing sampling schemes, because the contribution of each stage to the overall variance can be examined; it already appears in a number of ISO (International Standards Organization) sampling Standards (*e.g.*, ISO 12743, 1998). Once the relative magnitudes of the variance components are known, efforts to reduce the overall variance can be focused in the right area.

3. COMPONENTS OF SAMPLING ERROR

A better understanding of the sources of sampling errors and how to eliminate sampling bias and minimize variance is obtained by splitting the total sampling error TE_i for a given sampling Stage i into a number of independent components as follows (Gy, 1982a; Pitard, 1993):

$$TE_i = FE_i + GE_i + QE2_i + QE3_i + WE_i + DE_i + EE_i + PE_i \tag{2}$$

where FE_i is the fundamental error, GE_i the grouping and segregation error, $QE2_i$ the long-range quality fluctuation error, $QE3_i$ the periodic quality fluctuation error, WE_i the weighting error, DE_i the increment delimitation error, EE_i the increment extraction error and PE_i the preparation error.

This equation is strictly applicable to sampling from moving streams, so not all of the above components of error apply to every sampling situation. For example, the long-range and period quality fluctuation and weighting errors do not apply to percussion and blast-hole sampling, but the fundamental error, increment delimitation, increment extraction and preparation errors do apply. The last three components require special attention, because they can result in the introduction of sampling bias. Fortunately, these biases can be eliminated by the use of correct sampling equipment and procedures. The others are largely random errors that can never be completely eliminated, but they can be reduced to acceptable levels by careful design of the sampling system.

3.1. Preparation error

Preparation errors in the sampling context are non-selective operations without change of mass, such as crushing, grinding, mixing, sample transfer, drying, *etc*. Typical errors include sample contamination, sample loss (*e.g.*, due to sample spillage), moisture loss and operator mistakes, such as mixing up sample labels. These errors can be eliminated using correct sampling equipment and practices. For example, sample cutters should be covered if necessary to prevent entry of extraneous material in the parked position and moisture samples should be prepared and weighed quickly to avoid change in moisture content. Care also needs to be taken to ensure that the finer particles are not lost in crushers or mills or during sample division due to excessive air flow from dust extraction systems installed in sample preparation laboratories.

3.2. Delimitation and extraction errors

Increment delimitation errors arise from incorrect geometrical definition of the increment to be taken, *i.e.*, not taking a complete column when sampling an ore deposit *in situ* or incorrect cutter geometry when sampling from a moving stream. Increment extraction errors occur when increments are not fully extracted, *i.e.*, sample material is lost. For example:

- When sampling an ore deposit using percussion drilling, the drill hole must have parallel sides (correct *delimitation*) and all the cuttings must be transported to the surface for subsequent sample division (correct *extraction*).
- When sampling an ore deposit using diamond drilling, the drill hole must have parallel sides (correct *delimitation*) and all of the core must be recovered (correct *extraction*).
- When sampling a blast hole cone, a complete sector of the cone of cuttings must be selected (correct *delimitation*) and all the cuttings in the sector collected (correct *extraction*).
- When sampling concentrate in a truck using a spear sampler, the spear must be pushed down to the bottom of the truck (correct *delimitation*) and the complete increment extracted without any loss of concentrate from the spear (correct *extraction*).
- When sampling from moving streams, all parts of the stream cross-section must be diverted by the sample cutter for the same length of time (correct *delimitation*) and the increment must be completely extracted without any material rebounding or being lost from the cutter (correct *extraction*).

3.3. Weighting and periodic quality fluctuation errors

The weighting error largely relates to sampling from moving streams and is usually not a major problem. It arises from variations in the flow rate of the stream, so that individual increments do not carry with them the correct weighting information when they are combined into partial samples and gross samples, particularly for time-basis sampling. However, the problem can be overcome by regulating the flow rate prior to sampling.

Periodic quality variations also relate to sampling from moving streams and may arise from bucket-wheel reclaimers, pumps, *etc*. Difficulties arise when the sampling interval approaches that of the periodic variation and the taking of increments is in phase with the periodic variations. For example, when a bucket-wheel reclaimer is traversing the face of a stockpile, the centre and edges of the stockpile usually have different grades and particle size distributions. Hence, if increments are taken only when the reclaimer is at the edge of the stockpile, the resulting composite sample will be biased. Consequently, such sampling situations should be avoided unless increments are taken at random within each time or mass interval selected for sampling.

3.4. Fundamental error and minimum sample mass

The fundamental error is a critical consideration in designing any sampling scheme, whether it is for sampling drill holes, process streams, trucks or wagons. It results from the differences in composition between the individual particles being sampled, and as a consequence, for a given particle size, there is a minimum mass of sample, m_S, that must be retained after division to obtain acceptable precision.

Determination of this minimum mass is covered in considerable detail by Pitard (1993, Chapter 19) for both liberated and non-liberated gold. Useful sampling nomograms are also included for determining the minimum sample mass as a function of the size of the gold particles and the average gold grade for a range of fundamental errors. The sample mass cannot be reduced below this minimum, called the division limit, until the sample is crushed to a smaller particle size. This is a very important sampling rule, which unfortunately is often ignored to reduce the masses that sampling personnel need to handle, but it leads to poor sampling precision.

4. PERCUSSION HOLE SAMPLING

The mass of cuttings extracted from percussion holes is generally quite manageable, so it is possible to collect all the cuttings for subsequent sample preparation. The best method is to use reverse-circulation drilling to automatically collect the cuttings, where compressed air is pumped down the drill hole to force the cuttings up the centre of the drill stem and through a cyclone. The cuttings are then passed through a suitable divider, *e.g.*, a riffle (see Fig. 1) or cone divider, to extract a sample of appropriate mass. However, a substantial amount of dust (the finer particles) can bypass the sampling system and go directly to the dust filter, and substantial material build-up can occur on the sample divider, particularly when the drill cuttings are wet, which interferes with its operation. In addition, some sample dividers

Fig. 1. Riffle divider underneath a cyclone for division of drill cuttings.

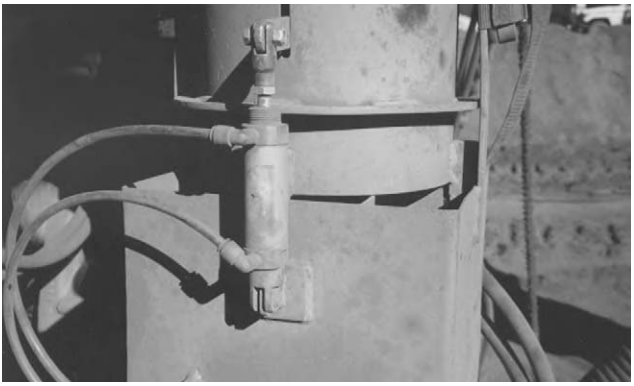

Fig. 2. Incorrectly designed sample divider on the side of a drill rig that collects material from only one side of the stream of cuttings (see slots on right-hand side of rectangular sample division device).

do not conform to correct sampling principles, *e.g.*, by collecting only one side of the stream of cuttings from the bottom of the cyclone (see Fig. 2). Sampling systems that collect only part of the cuttings from the drill hole for subsequent sample division should be avoided at all cost.

5. BLAST-HOLE SAMPLING

Blast-hole sampling practices have changed relatively little in recent years and continue to be problematic. Analyses of the samples collected are becoming increasingly important for grade control, however, as mining companies continue to push down operating costs by reducing the number of mining machines, the size of blending stockpiles and sample stations in the processing plant. This places much more pressure on the operators to feed ore of the required grade to the primary crusher, which in turn requires better estimates of the grades of ore blocks that are derived from blast-hole analyses.

When the diameter of blast holes is relatively small (below ~200 mm), the total mass of the drill cuttings is at least manageable and there are three main methods of taking samples. The first method is to take one or a number of complete sectors of the cone of cuttings surrounding the blast hole using *sector cutters* (see Fig. 3). This ensures that the cuttings from successive depth intervals are equally represented in the sample, assuming that no substantial cavities are created in the drill hole and loss of drill cuttings as dust is minimal. The sample cutter can also be removed prior to *sub-drilling* the bench, thereby avoiding contamination of the sample with sub-drill material.

The second method is to manually take two complete radial cuts from the blast-hole cone at 180° spacing after drilling has been completed and divide the cuttings down to an appropriate mass on-site using a riffle. There are several technical difficulties with this approach. Radial cuts, rather than being sector shaped, generally have parallel sides. Also, making allowance for sub-drill cuttings by removing the top of the blast-hole cone can be problematic. However, the accuracy of this approach is superior to the more

Fig. 3. Example of a manual sector cutter for sampling blast holes.

conventional approach of taking vertical cuts from near the centre of the blast-hole cone, as used for larger diameter blast holes.

The third method is to use an automatic vacuum extraction system and cyclone on the drill rig to pick up the cuttings around the top of the blast hole and pass them through a suitable divider, such as a riffle or cone divider, to extract a sample of appropriate mass. In principle, this approach sounds good, but in practice a substantial proportion of the cuttings are left around the blast hole (usually the coarser particles). A substantial amount of dust (the finer particles) completely bypasses the sampling system and goes directly to the dust filter, and substantial material build-up occurs on the sample divider, particularly when the drill cuttings are wet. Once again, some of the sample dividers do not conform to correct sampling principles.

As for percussion holes, the best approach is to use reverse-circulation blast-hole drilling to automatically collect the cuttings (see Fig. 4). The drill hole is sealed immediately behind the drill bit to keep the face of the drill hole dry so that a dry sample can be collected to prevent blockages in the sampling system on the drill rig.

For larger diameter drill holes (~300 mm), the total mass of the drill cuttings is very large, on the order of several tonnes. As a result, the masses of complete sectors of the cone are also very large (hundreds of kilograms), which creates serious material handling problems. Consequently, manual samples are commonly collected by digging a trench into the side of the cone of cuttings and taking vertical slices of cuttings near the apex of the cone, often at two positions approximately 180° apart around the cone. This approach is far from satisfactory due to radial segregation of the drill cuttings and lack of uniformity in the thickness of cuttings as they are deposited around the drill hole. To allow for drilling below the design depth of the bench, removal of a section from the top of the cone of drill cuttings prior to sampling is once again no more than a wild guess. Hence, it is virtually impossible to take representative samples from individual blast holes by taking vertical slices. Better approaches are as follows:

- Taking two complete radial cuts from the blast hole cone 180° apart after drilling has been completed and divide the cuttings down to an appropriate mass on-site using a suitable divider.
- Installation of an automatic vacuum extraction system on the drill rig to pick up the cuttings around the top of the blast hole and pass them through a suitable divider to extract a sample of appropriate mass.

The first option is very labour intensive, although a substantial part of the cone is removed when the *vertical slice* sampling method is used, so the additional effort is not as great as might first be thought. The second option

Fig. 4. Automatic sample extraction system mounted on a reverse-circulation blast-hole drill rig, which utilizes a cone divider for sample division.

has all the problems outlined above for smaller diameter blast holes, so substantial improvements in engineering design are required before it becomes a practical option.

6. PLANT SAMPLING

By far the best way of sampling a moving stream of ore, concentrate or slurry is using a correctly designed sample cutter at the discharge point of a conveyor belt, chute or slurry pipe. The stream can be intersected at preselected times or tonnages, and representative samples, or increments, can be collected by taking a complete cross-section of the stream with a sample cutter (Gy, 1982a, b; Pitard, 1993; Holmes, 1997, 2002, 2004), thereby eliminating the increment delimitation and extraction errors. A schematic of a suitable falling stream cutter taken from an Australian sampling standard

(AS 4433.1, 1997) is shown in Fig. 5. On the other hand, sampling devices that take only part of the stream, *e.g.*, a bleed from a slurry pipe in a concentrator, are likely to introduce serious bias and are not recommended.

When sampling from moving streams, the stream is divided into strata of equal time or mass, and increments are then taken from a fixed point of time or mass in each stratum (*systematic sampling*) or at random within each stratum (*stratified random sampling*). However, if periodic variations in quality are present in the stream, stratified random sampling should be used to eliminate possible bias.

For mass-basis sampling, the increment masses should be almost uniform to ensure that each increment carries the correct weighting information, for example, by using a variable speed cutter that adjusts its speed increment by increment so that it is proportional to the flow rate at the time the increment is taken. For time-basis sampling, the increment mass must be proportional to the flow rate, so a fixed speed cutter is required. Unless these conditions are met, weighting errors will be introduced. Time-basis sampling is the easier to implement, but variations in flow rate should not be excessive, otherwise the increment mass may not be proportional to the average flow rate during the sampling interval.

Sample cutters for sampling moving streams must satisfy the following design rules to eliminate increment delimitation and extraction errors:

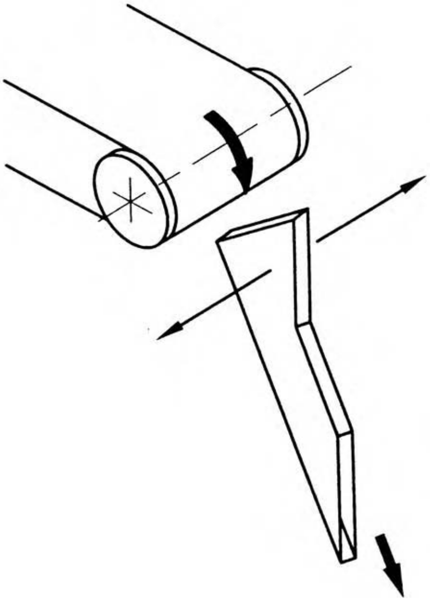

Fig. 5. Schematic of a falling stream sample cutter (from AS 4433.1, 1997).

- The cutter must collect a complete cross-section of the stream, both the leading and trailing edges of the cutter (lips) completely clearing the stream at the end of each traverse. Cutters that collect only part of the stream on a continuous or periodic basis, *e.g.*, *shark-fin* cutters (see Fig. 6), *pressure-pipe* samplers, T-pieces or *bleeds* from the side of a pipe (see Fig. 7), must be avoided at all costs.
- The sample cutter must be non-restrictive and self-clearing, discharging completely each increment without any reflux, overflow or hang-up. This is particularly important for *reverse-spoon* type cutters, where the ore, concentrate or slurry has to change direction as it strikes the back of the cutter body, otherwise sample reflux may occur. These comments also apply to *shark-fin* cutters in mineral concentrators, although they are usually fixed in position as well, which is also incorrect as already discussed above. Generously large cutter bodies and chutes are therefore required to avoid reflux and overflow from the cutter aperture. For sticky materials, steep chute angles ($>60^\circ$) and stainless-steel or polythene chute linings are recommended to reduce adhesion, and the cutter aperture may also need to be enlarged to prevent bridging.
- The geometry of the cutter opening must ensure that the cutting time at each point in the stream is equal. Hence, for linear-path cutters, the cutter edges must be parallel, while for cutters travelling in an arc, such as *Vezin* cutters, the cutter lips must be radial. Flap or diverter type cutters are always incorrect in this regard, because they divert one side of the stream for a longer period than the other (see Pitard, 1993).
- The cutter should intersect the stream either in a plane normal to, or along an arc normal to, the mean trajectory of the stream.

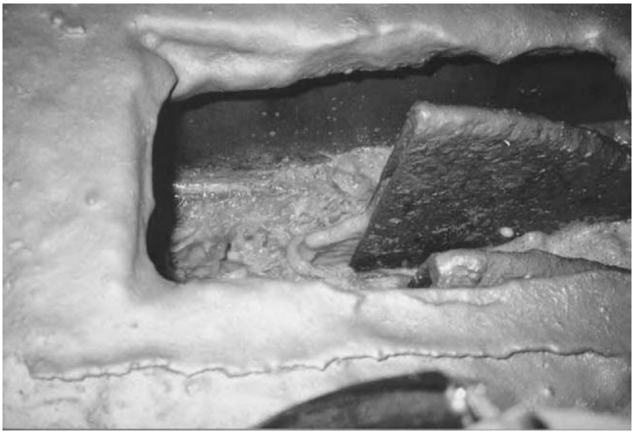

Fig. 6. *Shark-fin* cutters are unsatisfactory sampling devices, because they do not take a full cross-section of the slurry stream.

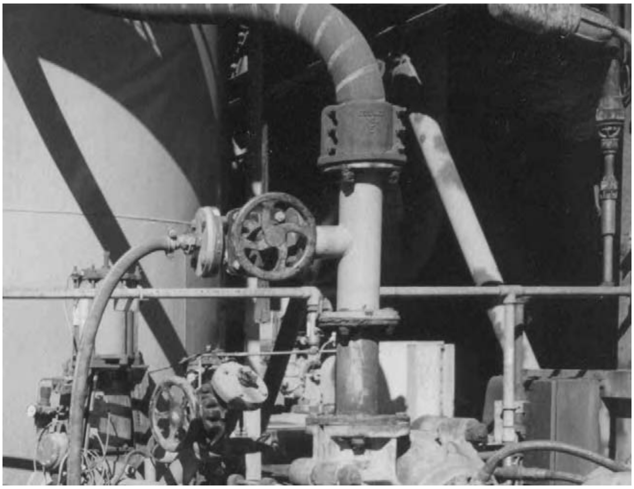

Fig. 7. Taking a *bleed* sample from a T-piece on a pipe in a concentrator is poor sampling practice and will not provide a representative sample.

- The plane of the cutter lips must not be vertical or near vertical, because particles that strike the inside edge of the cutter lips, and which should appear in the sample, are deflected away from the cutter aperture by gravity into the reject stream.
- The cutter must travel through the stream at a uniform speed, accelerating up to its cutting speed before entering the stream and then decelerating to a stop after leaving the stream. The cutter drive must also have sufficient power to ensure that the cutter does not slow down as it enters the stream and speed up as it leaves the stream.
- The cutter aperture must be at least three times the nominal top size (d) of the ore or concentrate being sampled to prevent preferential loss of the larger particles, subject to a minimum of 10 mm for slurries and fine dry solids. For wet solids, a minimum of 50 mm is recommended to stop bridging.
- Bucket-type cutters must have sufficient capacity to accommodate the increment mass obtained at the maximum flow rate of the stream without any reflux or overflow of material from the cutter aperture.
- No materials other than the sample must be introduced into the cutter or the sample delivery chute. If necessary, both need to be covered when the cutter is parked between increments to eliminate ingress of dust or spillage.
- If a belt scraper is required to remove material adhering to the belt, the scraped material must fall within the area traversed by the cutter.
- When sampling slurries, the cutter lips must be sharp and the sample cutter streamlined to minimize turbulence as it cuts the slurry stream (Bartlett, 2002). In addition, loss of sample material due to dribbling must be avoided. For

example, pipes must be bent to prevent slurry flowing back along the outside of the pipe, and the slope at the end of a launder must be sufficient to prevent slurry flowing back underneath the launder.

While both cross-stream and cross-belt cutters are used in industry for sampling ore and concentrate from moving streams, cross-stream cutters are recommended for two principal reasons. Firstly, cross-belt cutters tend to leave a layer of material on the conveyor belt if the skirts at the bottom of the cutter are not correctly adjusted as they gradually wear out or alternatively, maintenance staff tend to increase the gap due to fears of damaging the conveyor belt, so the increment extraction is incorrect. Consequently, cross-belt cutters can be seriously biased, because the material on the bottom of the belt is usually different in grade from the bulk of the material on the conveyor belt. Secondly, it is virtually impossible to check visually whether a cross-belt cutter is performing correctly. In contrast, cross-stream cutters can be checked visually during operation to confirm correct increment delimitation and extraction, and visual inspections are far more economically effective than conducting statistically sound bias tests.

The cutter speed is important for cross-stream cutters and Gy and Marin (1978) showed that it should not exceed 0.6 m/s at the minimum cutter aperture w_0 ($3d$ or 10 mm, whichever is the greater) to avoid extraction bias. However, if the cutter aperture (w) is increased above this minimum, the maximum cutter speed (v_c) can be increased as follows, subject to an absolute maximum of 1.2 m/s:

$$v_c = 0.3(1 + w/w_0) \tag{3}$$

Cutters can be found in mineral processing plants with speeds in excess of these limits to reduce the sample mass collected. However, the effective cutter aperture decreases as the cutter speed increases, and this can preferentially exclude the coarser particles and thereby introduce bias.

The *increment mass* m_I (kg) taken by a cross-stream cutter is determined by the *cutter aperture A* (m), the *cutter speed* (v_c) and the *stream flow rate G* (t/h) as follows:

$$m_I = GA/(3.6v_c) \tag{4}$$

Consequently, for a given flow rate, the minimum increment mass that can be correctly taken to avoid bias is determined by the minimum cutter aperture and the maximum cutter speed. It is not possible to take unbiased increments of smaller mass unless the flow rate is reduced or the ore is crushed prior to sampling so that the cutter aperture can be reduced accordingly.

A very useful parameter for checking the design and operation of sample cutters is the *extraction ratio*, which is the ratio of the actual increment mass collected to the theoretical increment mass calculated using Eq. (4). If this ratio is significantly less than 1, then the cause needs to be identified and corrective action taken to rectify the problem, *e.g.*, reflux of ore from the cutter aperture or hang-up in the cutter chute due to capacity problems or blockages in the cutter chute. The extraction ratio should be determined as a function of flow rate, because problems with reflux become more serious as the flow rate increases.

7. SAMPLING FROM STATIONARY SITUATIONS

7.1. Sampling from stockpiles

While taking representative samples from a stockpile may at first sight appear straightforward, this process is at best very difficult and often impossible. Samples are commonly taken from the side of the stockpile with a shovel or scoop (see Fig. 8), but it is not even remotely possible that all parts of the ore or concentrate in the stockpile have an equal probability of being collected, particularly in the centre of the stockpile. The samples taken will at best represent only the surface layers of the stockpile and will not be representative of the entire stockpile. An acceptable method is to use an auger or a spear sampler, but the implement must penetrate to the bottom of the stockpile and the complete column of material extracted without sample loss. For large stockpiles and for coarse material, this is virtually impossible. The best method of sampling a stockpile is to take samples from a moving stream as the stockpile is being built up or broken down.

7.2. Sampling from trucks and railway wagons

Because of their smaller size compared to stockpiles, it is possible to sample fine concentrates (<1 mm particle size) *in situ* in trucks and railway wagons using a spear sampler (see Fig. 9). However, several increments must be taken from each truck or railway wagon and the spear must penetrate to the bottom of the truck or railway wagon with the full column of concentrate extracted by the spear. This is possible for damp fine concentrates, but not for dry concentrates or lumpy ores.

7.3. Sampling from holding tanks and vessels

As for the other stationary sampling situations described above, it is impossible to reliably extract representative samples of solids or slurries *in situ* in holding tanks and other vessels using a ladle. There is bound to be some segregation in the vessel, particularly for slurries, where the coarser and denser particles tend to settle towards the bottom. The only acceptable ways

Fig. 8. Sampling from the side of a stockpile with a scoop will not provide a representative sample.

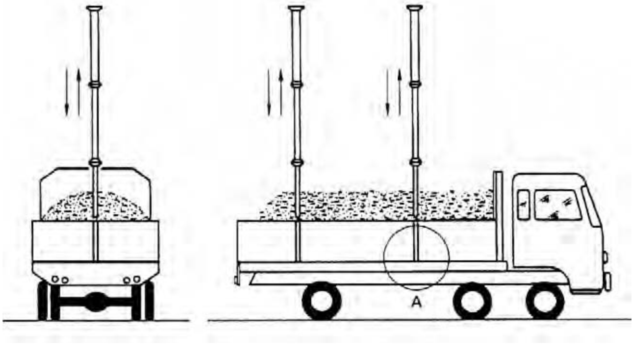

Fig. 9. Example of spear sampling from a truck (from ISO 12743, 1998).

of extracting representative samples are as follows:

- Full-depth sampling in which a number of full vertical columns are extracted from the vessel (usually impossible).
- Sampling from moving streams as the vessel is filled or emptied.

Of the above options, the second method is by far the best.

8. SAMPLE PROCESSING

After collection, samples may be processed individually or combined into gross samples if necessary. In both cases, they are crushed, dried and divided as necessary in a number of smaller scale sampling stages to produce test samples. At each of these stages the aim is to maintain the overall variance at an acceptable level and minimize bias. As already discussed above, for a given particle size, there is a minimum mass of sample that must be retained after division to obtain the required division variance. A common fault during sample processing is to reduce the sample mass too far before crushing and grinding, resulting in unacceptable overall variance. Other problems that can occur and can be eliminated through proper training of sample preparation personnel include:

- Discarding part of a sample prior to division, because it is too heavy to lift or carry.
- Incorrect use of sample dividers, particularly riffles, resulting in bias.
- Sample contamination due to inadequate cleaning of equipment between samples.
- Sample loss via the laboratory dust extraction system.

Suitable methods for sample division include rotary sample division, riffle division, strip division and manual increment division. Of these, rotary sample division is the most reliable method, provided a minimum of 20 rotations of the carousel occur during division, followed by riffle division. The variance of riffle division is generally larger than for rotary sample division, particularly in the hands of unskilled operators. However, the variance can be minimized by spreading out the sample to be divided along the length of one of the sample collection trays and then dividing it into two by pouring the sample uniformly into the middle of the riffle slots with the tray parallel to the long axis of the riffle. One of the two divided samples should be selected at random in order to avoid introducing bias, taking care not to leave any material remaining in the slots of the riffle divider.

9. CONCLUSIONS

Accurate sampling methods are critical to obtaining meaningful analytical data in the gold industry. The basic rule for correct sampling and sample processing is that all parts of the ore, concentrate or slurry being sampled must have an equal probability of being collected and becoming part of the final sample for analysis. If this is not the case, bias is easily introduced that cannot be eliminated by simply averaging replicate measurements. Special care must also be taken to ensure that sample masses are adequate at each stage of sampling and sample preparation to achieve the required precision.

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Chapter 2

Mineralogical investigation of gold ores

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Mineralogical investigation is a critical and integral aspect of any pre-feasibility study as well as one of the quality control measures in the process optimization step (Gasparrini, 1993; Marsden and House, 1993). Mineralogical information must be considered in conjunction with the metallurgical testwork program results to ensure that appropriate processing methods are evaluated and that the optimum processing technology and flowsheet methods are selected and incorporated into the final plant design. A table of mineral formulae is provided at the front of this book.

Mineralogical investigation of tailings and other streams from operational plants has two specific objectives. The first is to determine reasons why design efficiencies are not being achieved and the second is to provide insight for continued process optimization by identifying opportunities and the means to augment recovery (Chryssoulis, 2001). Gold deportment analyses also assist in setting realistic targets for tailings grade, which is the absolute measure of metallurgical performance.

A gold deportment study consists of two parts, the first involves a complete gold mineralogical distribution in which all *forms* and *carriers* of gold (for definitions see Section 1) are identified and quantified, while in the second the focus is on determining and ranking the causes for the gold losses. As each form and carrier of gold is independently assessed, the completeness of the gold mineralogical distribution is measured by the relative deviation of the mineralogical gold tally from the assayed value. A 10% deviation is considered acceptable for gold concentration in the range 0.02–1 g/t. This approach is considered more accurate and comprehensive than the diagnostic

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leaching method (Tumily, *et al.*, 1987), which is used more routinely as a first line of control and enables the relatively rapid turnaround of process-based leachability information.

The process mineralogy of gold is not limited to the gold minerals, submicroscopic gold and their carriers, but also includes the study of gangue minerals and other species that may affect gold processing, such as cyanicides.

1. GOLD MINERALOGY

1.1. Gold minerals and alloys

Gold is the most inert metal; consequently there are not many naturally occurring gold compounds, as listed in Table 1. The predominant occurrence is as native metal frequently alloyed with silver (Boyle, 1979). When the silver content exceeds 20%, the alloy is called electrum, an unofficial but universally accepted term. Other gold alloys are rare and generally confined to specific ores; for example, the two copper gold alloys: auricupride [Cu_3Au] and tetra-auricupride [AuCu] are found in higher gold-grade porphyry copper ores (Kemess, BC, Canada). Gold alloyed with platinum group elements (PGE) is encountered in PGE ore deposits and maldonite [Au_2Bi] is more common in the higher temperature mesothermal gold deposits (Pogo, AL USA; Navachab, Namibia). After native gold and electrum, tellurides are the most common gold minerals followed by aurostibite [$AuSb_2$]. Calaverite [$AuTe_2$] and sylvanite [$(Au,Au)Te_2$] are the most common tellurides comprising a significant fraction of the gold assay in a number of gold deposits (Emperor, Fiji; KCGM, Australia; Kumtor, Kirghizstan; Kensington, AL, USA; Sunshine, Ladkusky, MO, USA). Somewhat unique characteristics of gold minerals that separate them from the other minerals include their high specific gravity, brightness (high reflectance) and hardness, the latter as measured on the Vickers scale (see Fig. 1). In addition to the gold compounds listed in Table 1, there are three important submicroscopic gold occurrences that cannot be ignored when considering processing options and recovery optimization. These are solid-solution gold, colloidal size particulate gold and surface-bound gold. Examples of some gold minerals are given in Plate 3 and Fig. 2; some gold mineral associations are illustrated in Plate 4.

1.2. Solid-solution gold

Solid-solution gold refers to gold that is atomically distributed in the crystal structure of sulfide minerals like pyrite and arsenopyrite. The first indirect reference to solid-solution gold was made by Bürg (1930), who used the term *invisible gold* to describe submicroscopic gold in pyrite from the Bradisor mine in Romania. Under this term falls both solid-solution and colloidal gold (discussed in the next section).

Table 1
Gold minerals

Native elements, alloys and metallic compounds	
Native gold (<20 mol% Ag)	Au
Electrum (20–80 mol% Ag)	(Au,Ag)
Palladian gold (porpezite)	(Au,Pd)
Rhodian gold (rhodite)	(Au,Rh)
Iridic gold	(Au,Ir)
Platinum gold	(Au,Pt)
Goldamalgam	(Au,Ag)Hg
Weishanite	$(Au,Ag)_3Hg_2$
Maldonite	Au_2Bi
Auricupride	Cu_3Au
Tetra-auricupride	AuCu
Hunchinite	Au_2Pb
Bogdanovite	$Au_5(Cu,Fe)_3(Te,Pb)_2$
Bezsmertnovite	$Au_4Cu(Te,Pb)$
Sulfide/selenite	
Uytenbogaardite	Ag_3AuS_2
Fischesserite	Ag_3AuSe_2
Petrovskaite	AuAg(S,Se)
Tellurides	
Calaverite	$AuTe_2$
Krennerite	$(Au,Ag)Te_2$
Muthmannite	(Au,Ag)Te
Petzite	Ag_3AuTe_2
Sylvanite	$(Au,Ag)_2Te_4$
Kostovite	$CuAuTe_4$
Montbrayite	$(AuSb)_2Te_3$
Nagyagite	$[Pb(Pb,Sb)S_2]$ [Au,Te]
Silicates/Other	
As chlorite[a]	$(Mg,Al,Fe)_{12}[(Si,Al)_8O_{20}](OH)_{16}$
Auroantimonate	$AuSbO_3$

[a] Kucha and Plimer (2001).

Solid-solution gold tends to concentrate preferentially in arsenopyrite, with a maximum reported concentration of 1.7% (m/m) (Cook and Chryssoulis, 1990). In the larger (>50 µm) arsenopyrite crystals it is usually inhomogeneously distributed, concentrating along growth bands, giving undisputed evidence for incorporation of gold in the arsenopyrite structure during crystal growth (Chryssoulis and Cabri, 1990; Oberthür *et al.*, 1997). More importantly, solid-solution gold is typically strongly enriched in the finer grained sulfides (<20 µm) and is therefore harder to liberate from arsenopyrite (Cook and Chryssoulis, 1990; Novgodorava, 1993).

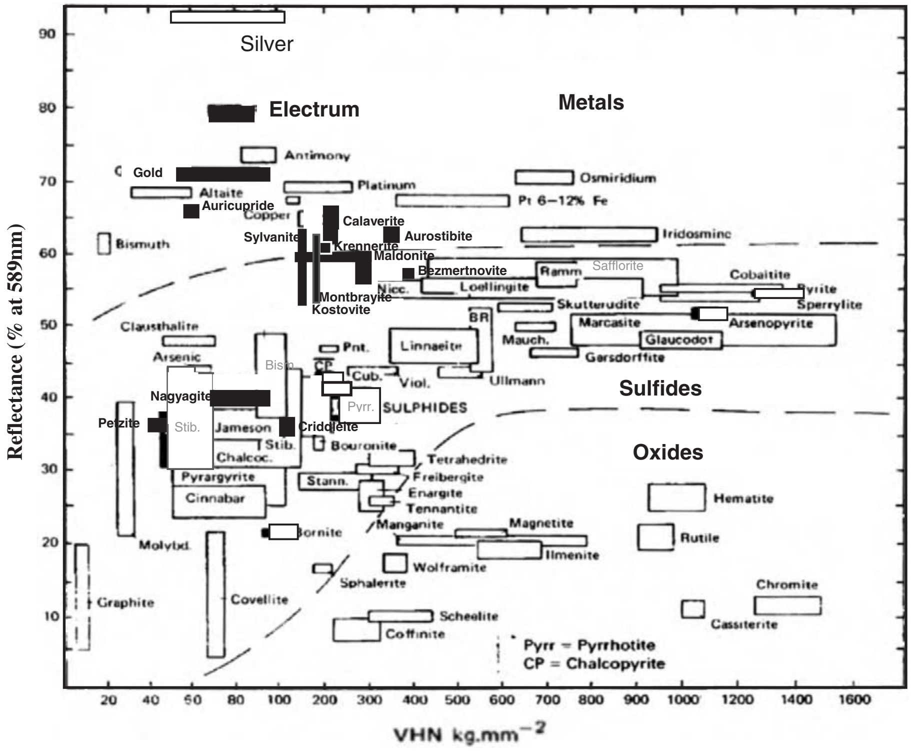


Fig. 1. Gold minerals highlighted in diagram of reflectance in air at 589 nm vs. VHN microhardness for ore minerals.

Pyrite is the most common of the sulfide minerals and may also incorporate significant amounts of gold in its crystal structure, to the point where solid-solution gold becomes the principal form of gold in the ore and pyrite its chief carrier (Thomas, 1997). Good examples are the disseminated sulfidic gold ores of the Carlin and Cortez Trends in Nevada (Wells and Mullens, 1973), the trend stretching across Northwestern China into Kirghizstan and Kazakhstan, and the trends along the Northwest Sichuan depression and the Youjiang basin in Southern China (Rui-Zhong *et al.*, 2002). The morphological types of pyrite pertaining to gold are illustrated in Fig. 3.

In ores with more than one morphological types of pyrite, solid-solution gold is usually confined to one or two types only, which is not surprising given their different origin (Arehart *et al.*, 1993a, b; Simon *et al.*, 1999). In mesothermal greenstone belt gold deposits solid-solution gold is hosted mostly by the coarser ($>50\,\mu$m) grained euhedral to subhedral pyrites. In epithermal deposits the finer ($<10\,\mu$m) grained and in particular microcrystalline

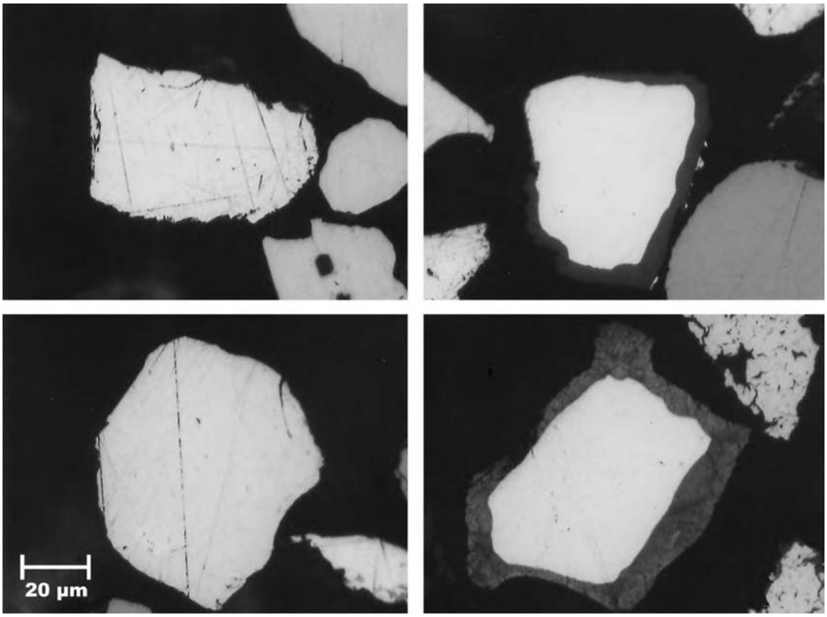


Fig. 2. Gold minerals (clockwise): calaverite [$AuTe_2$], aurostibite [$AuSb_2$] with aurostibate [$AuSbO_3$] coating, maldonite and maldonite with bismuth hydroxide [($Bi(OH)_3$] coating.

(<2 µm) pyrite is strongly enriched in submicroscopic gold. This effect is illustrated in Fig. 4.

The positive correlation between arsenic and gold concentrations in pyrite was recognized early in the course of routine determinations of solid-solution gold in pyrite by secondary-ion mass spectrometry (SIMS) (Chryssoulis and Cabri, 1990). The maximum solubility of gold as a function of arsenic content in pyrite is given by

$$C_{\mathrm{Au}} = 0.2C_{\mathrm{As}} \tag{1}$$

where C is the concentration of As, Au is in mol%. This is based on an Au vs. As plot (Fig. 5) of over 1000 microprobe analyses of pyrites of all morphological types from epithermal and mesothermal ore deposits (Reich *et al.*, 2004). They found that the maximum solubility of gold in pyrite from mesothermal deposits dropped by an order of magnitude (or one gold atom for every 50 arsenic atoms), as per the following equation:

$$C_{\mathrm{Au}} = 0.02C_{\mathrm{As}} \tag{2}$$

The chemical state and location of gold in the pyrite structure are still openly debated, but the consensus appears to be for aurous gold (Au^+) occupying iron sites, and As^{3+} providing the charge balance. It has been proposed that

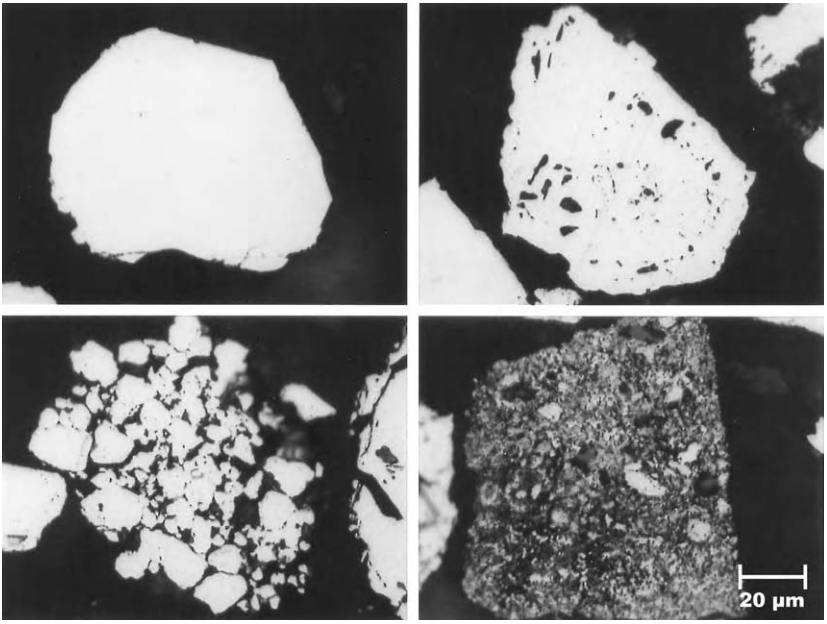


Fig. 3. Submicroscopic gold carriers: morphological types of pyrite (left to right) coarse, porous, fine-grained and microcrystalline. Porous pyrite can be host to colloidal gold, while maximum solid-solution gold concentrations are reported from microcrystalline pyrite.

the noted association of gold with arsenian pyrite could be the result of arsenic incorporation in the pyrite structure having created more p-type surfaces (Prokhorov, 1971), which would favour sorption of the electronegative gold radicals (Mironov *et al.*, 1981). Solid-solution gold in most cases is incorporated in the crystal structure of the host mineral during crystal growth; however, in one case (Ravenswood, NSW, Australia) it was diffused into the pre-existing pyrite structure along healed fractures.

Other minerals that may contain significant concentrations of solid-solution gold are loellingite (Pirila, Finland; Lupin, NWT, Canada), enargite (Chuquicamata and Pascua, Chile; Yanacocha, Perú) and tennantite (El Indio, Chile). Table 2 summarizes measured ranges of gold in various sulfide and arsenide minerals.

1.3. Colloidal gold

The term *colloidal gold* was introduced to describe discrete submicron gold inclusions in sulfide minerals, invisible by optical or conventional scanning electron microscopy (SEM), but detectable by SIMS in-depth concentration profiling (Chryssoulis, 1987) and also imaged and analysed by high-resolution transmission electron microscopy (HR-TEM) (Bakken *et al.*, 1989). Colloidal

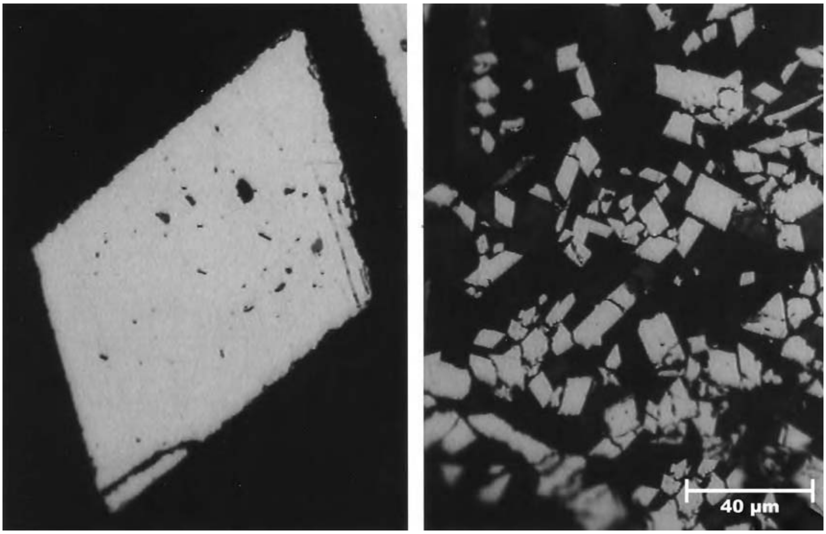


Fig. 4. Submicroscopic gold carriers: coarse and fine-grained arsenopyrite. A difference of 100–500 times on average (solid solution) gold content exists between the two morphological types, with the maximum reported gold content coming from the fine-grained arsenopyrite.

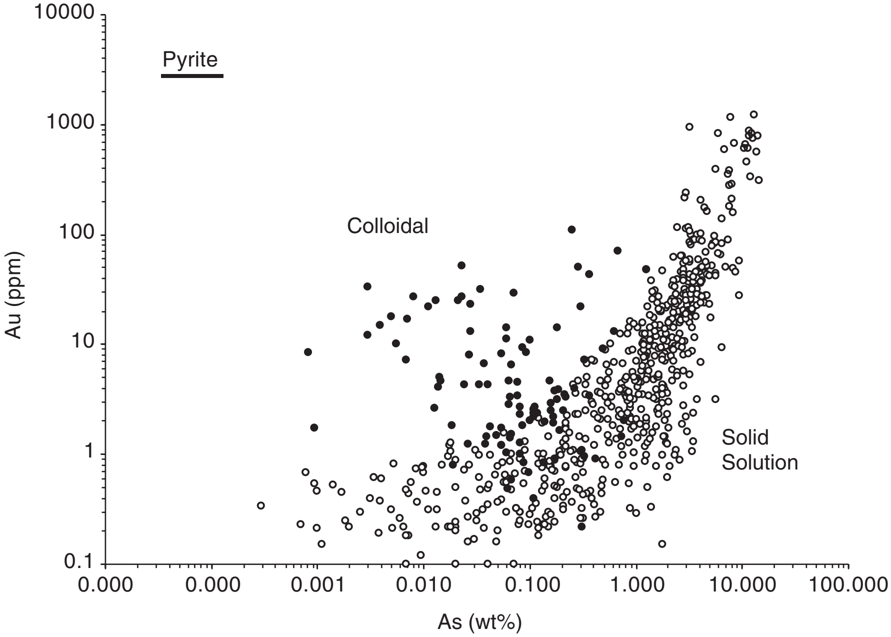


Fig. 5. Gold vs. arsenic plot for pyrite. Solid-solution gold (○) and colloidal size gold (●).

Table 2
Solid-solution gold concentrations in sulfides and sulfosalts

Mineral	Au (ppm)
Iron sulfides	
Pyrite	<0.1–8,800
Marcasite	<0.1–31
Pyrrhotite (roaster)	<0.1–5 (300)[a]
Arsenic minerals	
Arsenopyrite	<0.2–17,000
Loellingite	
Tennantite	<0.2–72
Enargite-Luzonite	0.3–62
Gersdoffite	<0.1–5
Realgar	<0.1–4
Orpiment	<0.1–3
Copper sulfides	
Chalcopyrite (synthetic)	<0.1–7 (44)
Bornite (synthetic)	<0.1–14 (360)
Covellite	<0.1–74
Chalcocite	<0.1–44
Antimony sulfides	
Tetrahedrite	<0.2–59
Stibnite	<0.1

[a] Synthetic.

gold "bridges" solid-solution gold and optical-microscope visible gold inclusions, thus demonstrating the continuity between these two forms of gold (Novgodorava, 1993).

Colloidal gold can be the product of exsolution of solid-solution gold or nucleation of adsorbed surface gold (Simon *et al.*, 1999). It also forms along the "reaction front" where a gold-barren sulfide is replacing a sulfide or arsenide-containing solid-solution gold (Chryssoulis and Weisener, 1994; Mumin *et al.*, 1994). Colloidal gold ranges in size between 5 and 500 nm, which is also the size range of *insols* in liquid colloidal solutions (Thiele, 1950). Colloidal gold is mostly spherical and is not necessarily confined to the sulfide matrix, as it has also been observed in the surrounding clay minerals (Bakken *et al.*, 1989). Colloidal gold also forms by coagulation during roasting where pyrite is oxidized to form magnetite, maghemite and hematite (Stephens *et al.*, 1990), and may also form during pressure oxidation and bioleaching.

The preferential host of colloidal gold is pyrite and to a lesser extent arsenopyrite. Unlike solid-solution gold there is no requirement for pyrite to be

Table 3
Maximum colloidal gold concentration in minerals

Mineral	Au (ppm)	Ore
Pyrite	15,500	Porgera, Papua New Guinea
Tetrahedrite	520	Lara, BC, Canada
Enargite	170	Pascua, Chile
Covellite	125	Chuquicamata, Chile
Chalcocite	29	Skouries, Greece
Bornite	33	Chuquicamata, Chile
Maghemite[a]	1,950	Goldstrike, USA
Hematite[a]	1,130	Goldstrike, USA
Goethite[a]	54	Goldstrike, USA

[a] Secondary formed by roasting gold-rich pyrite.

arsenian (arsenic-bearing typically with more than 0.5% As by mass). This is illustrated in Fig. 5; when pyrites with colloidal gold are depicted on an Au vs. As scatterplot they may plot above (Kirazli, Turkey) or below (KCGM) the line of maximum solubility of solid-solution gold in pyrite and there is no correlation with arsenic content (Screamer, NV, USA). Maximum colloidal gold concentrations for some minerals are given in Table 3. Colloidal gold is much more reactive than coarser grained gold because of its much higher specific area (surface/volume). This is evidenced by the rapid dissolution of gold at very low cyanide concentrations from autoclave discharge samples.

1.4. Surface gold

Surface gold refers to gold detected on the surface of mineral particles, the most classic example being gold adsorbed onto carbonaceous particles. Surface gold is the result of sorption, reductive deposition (plating), precipitation and possibly ion-exchange deposition from gold-bearing solutions. In roaster off-gas scrubbers it could be the product of volatile gold compound ($AuCl_2$, AuCl(CO)) condensation (Puddephatt *et al.*, 1989). The best examples of sorbed gold are gold preg-robbed by carbonaceous matter or loaded onto activated carbon (Adams and Burger 1998a, b). Dissolved gold is reductively deposited onto pyrite both in nature and during processing (Chryssoulis, 1997). Surface gold has been measured on carbonaceous matter from Cortez (NV, USA) in concentrations up to 15 ppm in the 12 nm surface layer analysed, corresponding to 1.7 g/t Au bulk concentration. Reductive adsorption of gold onto copper minerals was demonstrated by Adams *et al.* (1996).

In nature this preg-robbed surface gold occurs as three species, Au°, $AuCl_2^-$ and $Au(SCN)_2^-$ and this could be the mechanism by which gold becomes incorporated in the arsenian pyrite lattice as solid-solution gold or in arsenic-poor pyrite as gold micro-inclusions (Simon *et al.*, 1999). In the former, the reduction of gold is in all likelihood partial (Au^{3+} reduction to Au^{+}), while in the latter the reduction is complete to Au°. Precipitation of gold salts usually occurs to some extent in heap leaching operations. Finally, gold deposition by ion-exchange could be an alternative mechanism for incorporation of gold in the arsenian pyrite structure to that proposed by Reich, *et al.* (2004), who suggested that gold might be filling vacant iron sites that were created by the arsenic substitution. This ion-exchange mechanism for gold incorporation into pyrite is very hard to prove given the low gold concentrations involved. The only indirect evidence is replacement of As/Au-poor pyrite by As/Au-rich pyrite along fractures (Chryssoulis and Grammatikopoulos, 2003).

1.5. Forms and carriers of gold

The terms *form* and *carriers* of gold were introduced several years ago to better describe in a more collective manner the response of gold-bearing minerals to flotation. Thus, *form* of gold refers to the exact locus and chemical state of gold such as gold minerals as well as solid-solution, colloidal and surface-bound gold, while the term *carrier* of gold refers to the particles which host one or more forms of gold, thereby controlling response to flotation. An example of the latter is free gold vs. gold with pyrite which could also contain solid-solution/colloidal gold vs. gold in middling particles (Chryssoulis and Grammatikopoulos, 2003). This terminology has been found particularly useful in describing gold deportment in flotation tailings with a focus on recovery. In the case of leach tails, the term carrier loses its relevancy and what becomes more pertinent are terms like: exposed, enclosed and refractory.

2. PROCESS MINERALOGY OF GOLD

2.1. Gravity concentration

Mineralogical parameters affecting the recovery of gold grains by gravity (see Chapter 13 for more details on gravity concentration) are in order of decreasing importance:

- Particle size
- Degree of liberation
- Mineral density differential
- Particle shape
- Composition
- Hydrophobicity.

Fine free gold, which is too small to be recovered efficiently, depends on the installed equipment: 500 μm for sluices; 200 μm for jigs, 50–100 μm for spirals,

Table 4
Specific gravity of gold minerals

Gold mineral	Formula	Specific gravity (g/cm^3)[a]
Native gold	(0–20% Ag by mass)	16.4–19.3
Electrum	(20–50% Ag by mass)	13.2–16.4
Maldonite	Au_2Bi	15.7
Aurostibite	$AuSb_2$	9.9
Tetra-auricupride	AuCu	14.8
Calaverite	$AuTe_2$	9.2
Krennerite	$AuTe_2$	8.6
Sylvanite	$(AgAu)Te_2$	8.1

[a] Palache *et al.* (1944).

50 μm for shaking tables and 20–40 μm for centrifugal concentrators (Will, 1988). Association of gold with other minerals and in particular locking of fine gold grains in quartz and other 'light' gangue minerals reduces the average particle density. As an example a quartz particle with 14% (w/w) native gold has an average density close to that of pyrite (5 g/cm^3). The silver content of native gold and electrum reduces the density of the gold particle according to

$$\rho = 0.0007C_{\mathrm{Au}}^2 + 0.0177C_{\mathrm{Au}} + 10.517 \qquad (3)$$

(where C_{Au} is the gold concentration in % (m/m)) thereby also reducing the density differential with the other minerals. The density of some of the gold minerals is given in Table 4. Since gold metal is very ductile and malleable, free gold grains become flattened, instead of breaking up during grinding and milling, and this will be more pronounced with larger gold grains. Flaky gold tends to "surf the bowl" in a centrifugal concentrator in a similar fashion to a sail in the wind, orientating itself parallel to the water flow in table concentrators thus increasing chances for rejection (Knipe and Chryssoulis, 2004). Hydrophobicity imparted on gold surfaces due to the adsorption of hydrocarbons and elemental sulfur can keep flaky gold floating in table concentrates thereby contributing to losses.

2.2. Floatability of gold minerals and carriers

Examination of rejected free gold grains from numerous flotation plants has led to the following ranking of parameters affecting gold mineral flotation (see Chapter 14 for more information on flotation):

- Size of gold grains outside normal floatable size classes.
- Silver content of native gold.

- Composition of gold mineral.
- Activators and depressants.
- Collector loading.
- Shape of gold grains (flaky vs. equant).

2.2.1. Size and shape of gold grains

Free gold grain losses to the slimes (<5 μm) fraction is the main cause of free gold rejection in flotation plants. Flotation efficiency drops rapidly for particles below 5–7 μm (see Fig. 6), with overgrinding frequently being the issue in regrind circuits (Chryssoulis *et al.*, 2004). It should be noted that gold slimes production and losses are pertinent to both primary grinding circuits (pre-flotation) and in regrind circuits which are integrated with the flotation cleaning circuits. Column cells have been shown both at Grasberg (Irian Jaya) and Kemess to efficiently recover finer size free gold (5–70 μm), while being less effective in recovering coarser (for example, see Plate 2) and in particular flaky gold (Chryssoulis *et al.*, 2003b). This results in the necessity for mechanical re-scavenger cells in the cleaner circuit. As in primary grinding circuits, gravity concentrators and unit cells, flash flotation and contact cell units have their place in regrind circuits. They do have the potential to significantly reduce losses by removing coarser gold before it becomes too flaky to be recovered efficiently. At Bulyanhulu, the introduction of a contact cell treating the Knelson tails resulted in a net 1.5–2% recovery improvement of the rougher flotation line. Both techniques (gravity and flotation) are complimentary in recovering gold particles of different size distribution.

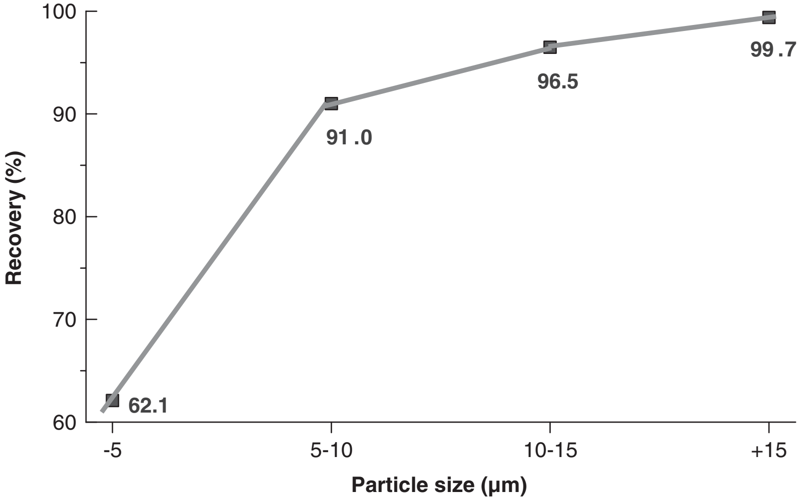


Fig. 6. Size by size recovery of fine free gold in cleaner circuit. Different flotation cells and configurations give different recovery curves.

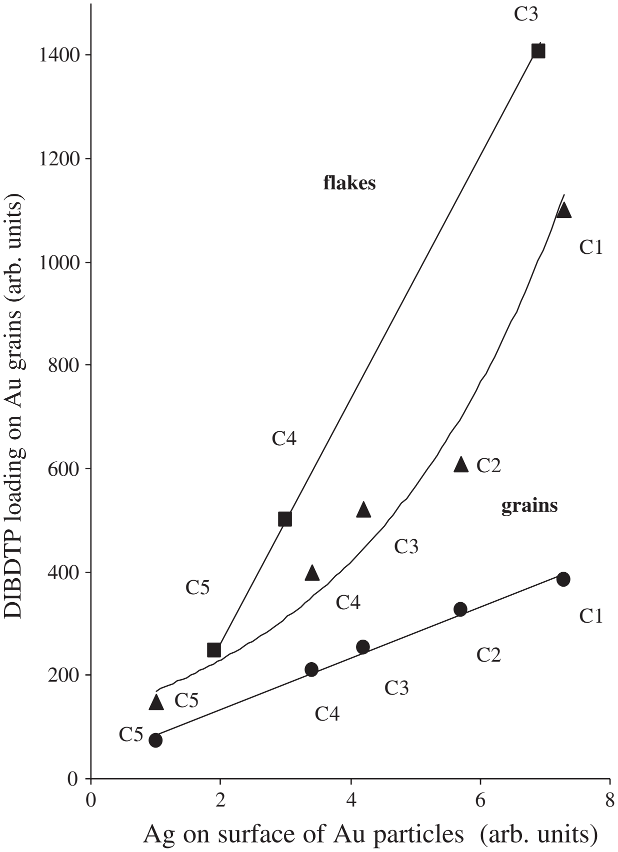


Fig. 7. Comparative di-isobutyl dithiophosphate (DIBDTP) loadings on gold grains with clean surfaces (●), gold grains with depressants (▲) and large (100–200 μm) clean gold flakes (■) from sequential concentrates (C1–C5).

On the other end of the gold grain size spectrum, coarser gold in the final tails (for example, see Plate 1) is invariably flaky. In order to float large gold flakes, heavier collector loadings are required compared to smaller equidimensional grains, as illustrated in Fig. 7 (Chryssoulis *et al.*, 2003a). In such cases a cost benefit analysis is required before implementing a gravity circuit.

2.2.2. Silver content of native gold

Several years ago, while examining the deportment of gold in the Phoenix gold project (NV, USA) it was discovered that silver-poor free gold grains were being lost preferentially. Since then in many flotation plants a differentiation has been documented based on the silver content of gold (see also Chapter 34). Some plants fell in line with Phoenix, while in others the exact opposite was observed, that is silver-rich free gold grains were lost selectively

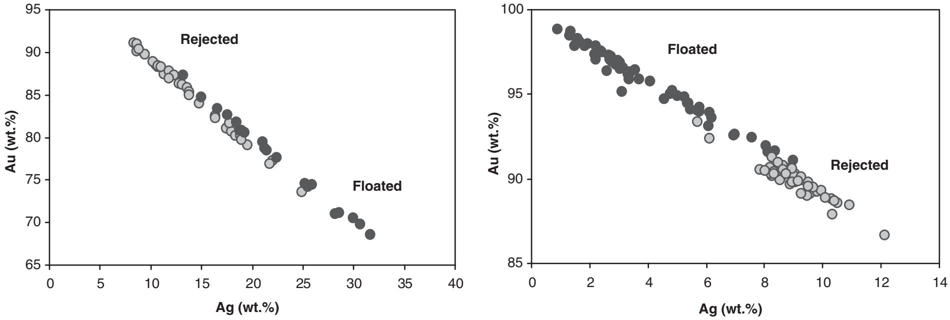


Fig. 8. Effect of silver on gold grain floatability; depending on the collector blend used either silver-rich (left plot) or silver-poor (right plot) gold grains are lost selectively.

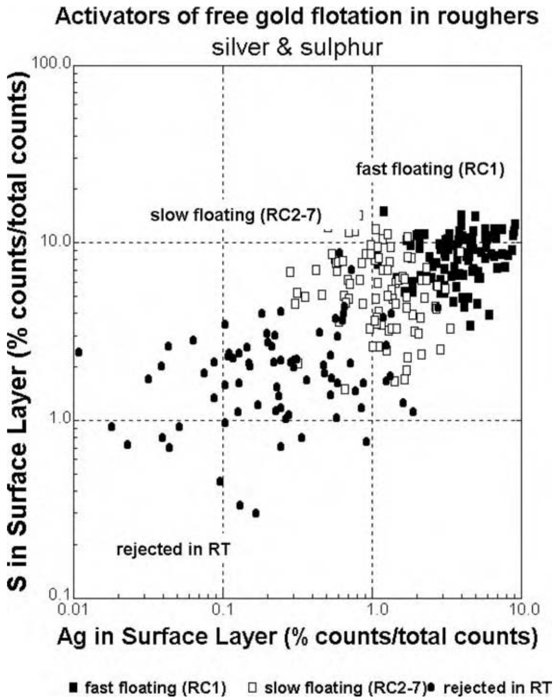


Fig. 9. Surface silver and sulfur on fast, slow and rejected free gold grains in the Bulyanhulu (Tanzania) rougher circuit.

(see Fig. 8). In some flotation plants, silver has a marked effect on free gold flotation kinetics as illustrated by the plot in Fig. 9. This led to the conclusion that the observed free gold flotation behaviour was affected by the collector blend used, and the concept of matching collectors to a particular silver content was introduced. Along the same lines, it was found that monothiophosphinates were better suited for silver-bearing gold (Basilio *et al.*, 1992). Nagaraj *et al.* (1992) documented the benefits of *di*crecylmonothiophosphate (DCMTP) in floating silver-poor gold.

2.2.3. Activators and depressants

Pure gold metal surfaces are naturally hydrophilic; however, the easy sorption of hydrocarbons imparts some hydrophobicity, resulting in some natural floatability. The oleophilic character of gold makes pine oil an excellent frother for gold collection. The natural floatability of gold invariably needs to be enhanced by the use of flotation collectors common to sulfide flotation. Based on extensive plant experience (Adams *et al.*, 2002) and more recently, surface analysis of gold–silver alloy metal plates (Basilio *et al.*, 1992; Nagaraj *et al.*, 1992), a number of collectors and formulated blends have shown marked superiority, although xanthates are still being used extensively. The effect of frother selection may also prove to be important.

Free gold losses within floatable size classes (7–150 μm) typically represent less than 10% of the gold in the final tails. Evidently, surface modifiers played a role in their rejection. Comparative statistical analysis of floated versus rejected free gold grains from 10 flotation plants (see Fig. 10) has shown that surface compositional changes can compromise gold floatability in a number of ways (Chryssoulis, 2001). Excessive sorption of hydroxyl and calcium ions is the most common cause for gold rejection, mainly in the cleaner circuit. This detrimental effect can be moderated by ramping up the pH in the cleaner banks and by adding collectors in the regrind at modest dosages to dress up the new surfaces produced. Despite the finer particle size in the regrind circuits, the use of flash flotation can assist gold recovery. For example, at Bulyanhulu, at a regrind of $P_{80}\sim 20\,\mu m$, the introduction of flash flotation improved gold recovery by 1.5–2.0%.

Other free gold depressants include carbonate, arsenate and phosphate species, some of which can be reverted to activators by sulfidization (NaHS). Iron hydroxide coatings hamper gold flotation but are hardly the main cause for free gold rejection. At Batu Hijau, manganese hydroxides were strongly enriched on the rejected free gold particles. In most flotation plants, sulfur and silver on gold grains (in all likelihood in the form of silver sulfide) promoted gold flotation. Copper must be assisting gold flotation as deciphered from the superior floatability of auricupride [Cu_3Au] and tetra-auricupride [AuCu] relative to native gold. At the Kemess flotation plant depending on the ore type (milled in separate campaigns) the role of some surface modifiers changes. In the presence of chloride ions, mercury in native gold can act as a depressant.

Rock/sulfide mineral binary particles, often referred to as middlings, can be significant gold carriers and warrant special attention in that contained gold

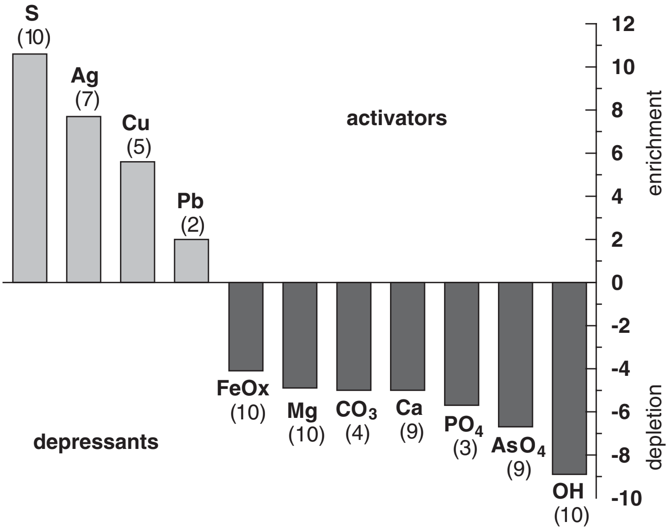


Fig. 10. Ranking of surface modifiers affecting gold floatability, based on comparative analysis of floated with rejected free native gold and electrum particles from 10 concentrators (Bajo de Alumbrera, Batu Hijau, Bulyanhulu, Cadia, Candelaria, Kemess, KCGM, Los Pelambres, Porgera and Troilus). Numbers in parentheses give frequency of occurrence.

grains can be more readily amenable for recovery that gold associated with pyrite, given the coarser size of the gold inclusions.

2.2.4. Collector loading

It is not surprising that by matching collectors to free native gold composition (see Fig. 11), gold flotation kinetics can be enhanced (Chryssoulis *et al.*, 2003a). Dixanthogen is an excellent collector of silver-poor native gold with clean surfaces. As the silver content of gold increases and inorganic surface contaminants build-up, dixanthogen loses its importance as a gold collector (Chryssoulis, 2005).

Given the limitations in efficiently floating gold grains in the slimes fraction, the build-up of surface contaminants (also referred to as particle surface aging) renders them even less floatable. This has been documented by comparative surface microanalysis of coarser and finer grained free gold, floated or rejected. The efficient performance of flash flotation is likely explained by this effect as flash flotation occurs in the early stage of liberation.

2.2.5. Composition of gold mineral

Of the gold minerals, calaverite [$AuTe_2$] floats more efficiently than metallic gold at KCGM (Western Australia) and Kumtor (Kirghizstan).

Pyrite and arsenopyrite are the principal hosts of submicroscopic gold. In addition, gold minerals are often preferentially associated with these

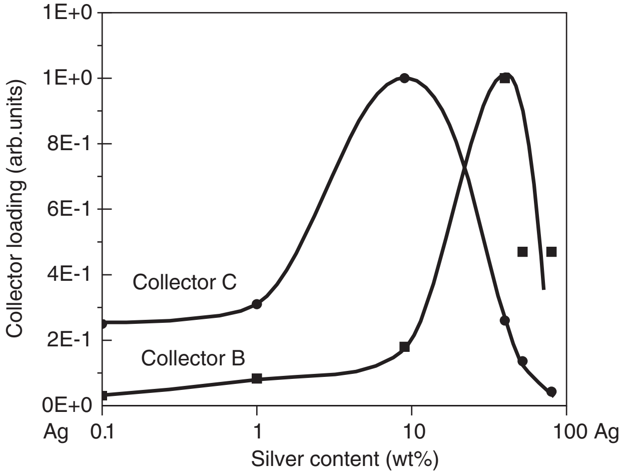


Fig. 11. Differential collector loading based on silver content of gold.

minerals; hence, their floatability is relevant to gold metallurgy. The following possibilities exist in the case of sulfidic gold ores:

- Bulk sulfide flotation for further treatment (ultrafine grinding (UFG) or pre-oxidation).
- Sequential flotation from gold-bearing base metal-sulfide ores.
- Separation of gold-bearing arsenopyrite from barren pyrite.

When attempting to concentrate submicroscopic and in particular solid-solution gold, it is important to keep in mind the following two peculiarities of the host sulfides:

- A strong correlation of gold with arsenic in pyrite.
- A strong enrichment of gold in the finer grained varieties of both pyrite and arsenopyrite.

Although the exact location of arsenic in the pyrite crystal structure is still being debated the general consensus is that arsenic is replacing one of the two sulfur atoms in the sulfur dipole, thus forming AsS^{2-}. Whatever the mechanism of arsenic incorporation in the pyrite structure, it is certain that with increasing arsenic content, pyrite becomes more readily oxidizable which in turn affects its floatability. Pure pyrite floats without activation because of dixanthogen formation as a result of catalytic oxidation of xanthate on clean (fresh) pyrite surfaces. However, most floated pyrite is either copper or lead activated which means that incipient surface oxidation had to take place to form *islands* of pyrrhotite, which then became sites for activation by Cu or

Pb. With increasing arsenic content, the surface oxidation of pyrite is greatly accelerated to the point where depression by surface oxidation overwhelms activation. This pyrite requires heavier collector loadings in order to float. If the oxidation is too fast, in the absence of activators irreversible depression takes place. Understanding the mechanism of arsenian pyrite flotation is particularly important given that it is the principal gold carrier in the very important submicron gold pyritic sedimentary-hosted gold deposits, also known as Carlin-type deposits (Thomas, 1997). To overcome the inadvertent oxidation of pyrite in the N2TEC process implemented at Twin Creek (NV, USA), grinding and flotation are carried out under nitrogen atmosphere using lead nitrate as the activating agent (Simmons, 1997). Barrick testwork on the Carlin ores demonstrated that the use of acidic flotation improved selectivity and kinetics. The success in maximizing recovery of gold-bearing arsenian pyrite from Carlin-type ores lies in minimizing unwanted pyrite oxidation coupled with generous activation, while producing lower grade sulfide concentrates by recovering middlings with finely disseminated gold-rich pyrite (see Fig. 12).

In the case of mesothermal pyritic gold ores, pyrite and arsenopyrite are sufficiently coarse grained, which allows for good liberation at modest grind fineness (P_{80} of 75–120 μm) and results in high-grade concentrates with good recoveries. In some of these ores, submicroscopic gold is exclusively carried by arsenopyrite, which makes separation enticing from the barren pyrite (Donlin Creek, AK, USA), while in others submicroscopic gold is equally shared by arsenopyrite and arsenic-rich pyrite (Olympias, Greece).

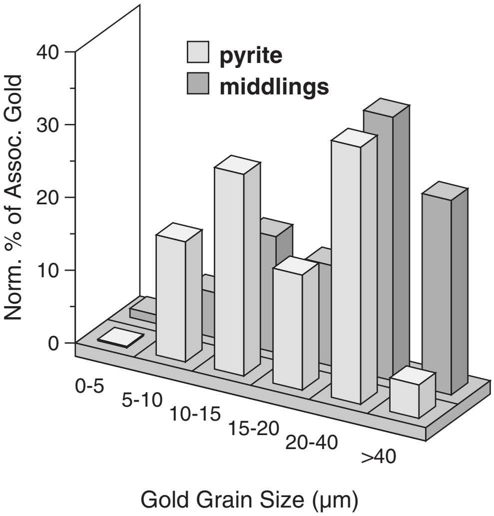


Fig. 12. Size distribution of gold associated with pyrite and middling particles.

Free gold recovery from the slimes fraction can be enhanced by adding some of the “best-match” collector in the regrind mill feed, to build up a heavier collector loading on already free tiny gold particulates as well as *coat* newly liberated gold grains when their surfaces are still fresh. In ores with gold grains displaying a bimodal or broad silver concentration distribution, a *matching collector* will enhance flotation kinetics of the slower floating member.

2.3. Leachability of gold minerals

2.3.1. Cyanidation in leach tanks

Of the gold minerals only native gold, electrum and auricupride are readily cyanidable, as listed in Table 5. Sylvanite [$AuAgTe_4$], calaverite [$AuTe_2$] and maldonite [Au_2Bi] are refractory to direct cyanidation under normal leaching conditions, requiring more aggressive tailored conditions to yield all or part of their gold content (Spry *et al.*, 2004); see also Chapter 20. Aurostibite [$AuSb_2$] converts into $AuSbO_3$ in alkaline solutions yielding no gold. Colloidal gold with iron hydroxyoxides in framboidal configuration is usually enriched in the tailings of leach plants indicating poor dissolution kinetics. Comparative surface microanalysis of free native gold and electrum grains from feed and leach tails of 12 plants identified a number of common surface species (see Fig. 13), which interfered with gold dissolution, hampering complete extraction of the exposed gold.

The numbers in parenthesis indicate the number of plants where a particular contaminant was found to be a problem (interestingly, in four plants lead could have had a detrimental effect on recovery; $PbNO_3$ is a common additive in plants leaching sulfidic gold ores, to enhance gold leach kinetics and recoveries).

The progressive build-up of surface species was documented by analysing gold grains down a train of agitated leach tanks, as well as from laboratory testwork with varying leach time (see Fig. 14). Surface species on residual free

Table 5
Response to direct cyanidation of the most common gold minerals

Gold minerals	Rate	Dissolution (%)
Native gold [$Au_{>0.8}\ Ag_{<0.2}$]	Fastest	100
Electrum [$Au_{<0.8}\ Ag_{>0.2}$]	Fast	100
Aurocupride [$AuCu$]	Fast	100
Sylvanite [$AuAgTe_4$]	Slow	100
Calaverite [$AuTe_2$]	Slow	>80
Maldonite [Au_2Bi]	Slow	0–20
Aurostibite [$AuSb_2$]	0	0
Auroantimonate [$AuSbO_3$]	0	0

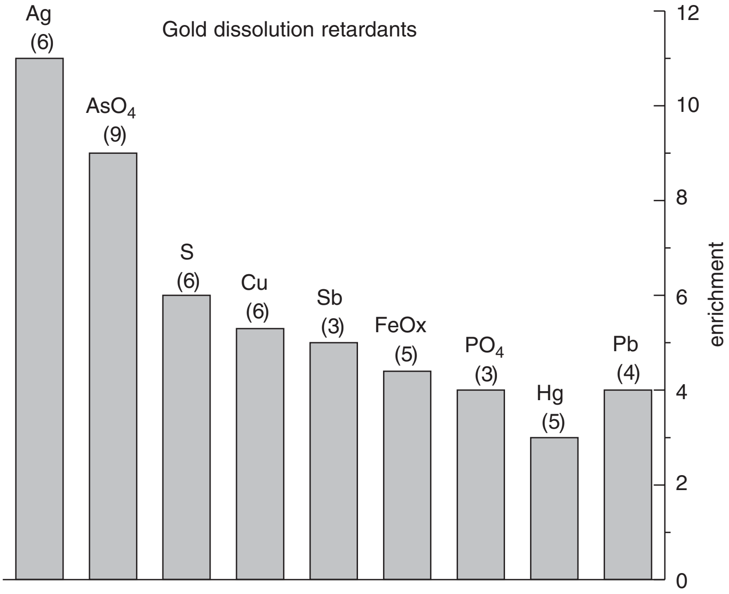


Fig. 13. Ranking of surface contaminants hampering complete gold dissolution, based on a comparative analysis of free gold from feed and leach residues of 10 cyanide leach plants (Big Bell, Waihi, Macraes, Cortez, Sadiola, Tarkwa, David Bell, Williams, Stawell and Sunrise Dam).

gold particles originates either from the gold grain itself or from the solution. Silver and mercury are good examples of elements that are commonly minor or trace constituents in gold. As the rate of silver extraction is only a fraction of that of gold (Barsky *et al.*, 1934), silver becomes progressively enriched on the surface of dissolving gold grains. Once such a layer is fully developed, covering entirely the gold particle, it will control the gold dissolution rate. Sulfide sulfur, arsenate and antimonite ions in solution adsorb onto gold grain surfaces, frequently reacting with silver to form sparingly soluble or insoluble compounds (see Plate 5).

Direct determination of the composition of the surface contaminant on residual free gold grains (Fig. 14) can unequivocally identify the cause of the problem, thus providing clues for the appropriate remediation action. As an example, the presence of silver antimonate, points to a pH value >11 (Hedley and Tabachnick, 1958) in the pre-aeration step and/or during leaching, which combined with a low free cyanide or dissolved oxygen concentration, promoted the build-up of silver, resulting in the reaction:

$$\underset{\text{on gold surface}}{3\text{Ag}} + \underset{\text{in solution}}{\text{SbO}_4^{3-}} \rightarrow \underset{\text{on gold surface}}{\text{Ag}_3\text{SbO}_4} + 3\text{e} \qquad (4)$$

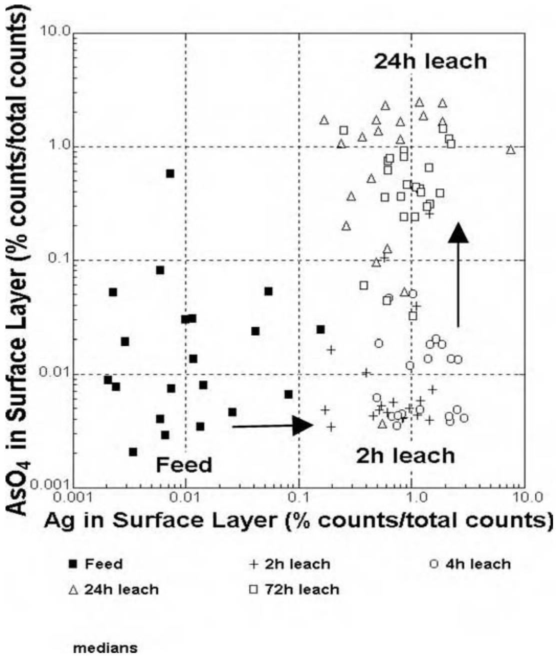


Fig. 14. Build-up of silver and arsenate on residual gold grains after 2, 4, 24 and 72 h cyanide leaching. Each point is a median of five surface measurements per particle.

An analogous mechanism is envisaged for silver arsenate (Venter *et al.*, 2004) with the antimonite and arsenate originating from the oxidation of minerals such as stibnite [Sb_2S_3], gudmundite [FeSbS], berthierite [$FeSb_2S_4$], arsenopyrite [FeAsS] and arsenian pyrite [As-FeS_2]. Mercury is another element that will accrue on the surface of residual gold (Chryssoulis and Winkers, 1996), hampering its timely extraction, because like silver at normal cyanide concentration levels, it dissolves at a slower rate than gold. The fix, albeit not always, to many of these problems is conditioning with lead nitrate. Lead forms very insoluble compounds with sulfidic sulfur arsenate and phosphate, thus removing them from solution before they reach the gold grain surface and interfere with dissolution.

Preg-robbing by carbonaceous matter seriously hampers gold extraction by direct cyanidation, requiring in most cases roasting or the use of alternative lixiviants (see Chapter 38). Surface gold on carbonaceous matter from unleached ore samples (Cortez, NV, USA) is evidence for sorption from gold-bearing hydrothermal solutions (natural preg-robbing). Significant care has to be exercised during analysis to avoid micrometer size gold-rich arsenian pyrite inclusions in the carbonaceous matter. SEM images of activated carbon and carbonaceous matter are shown in Fig. 15.

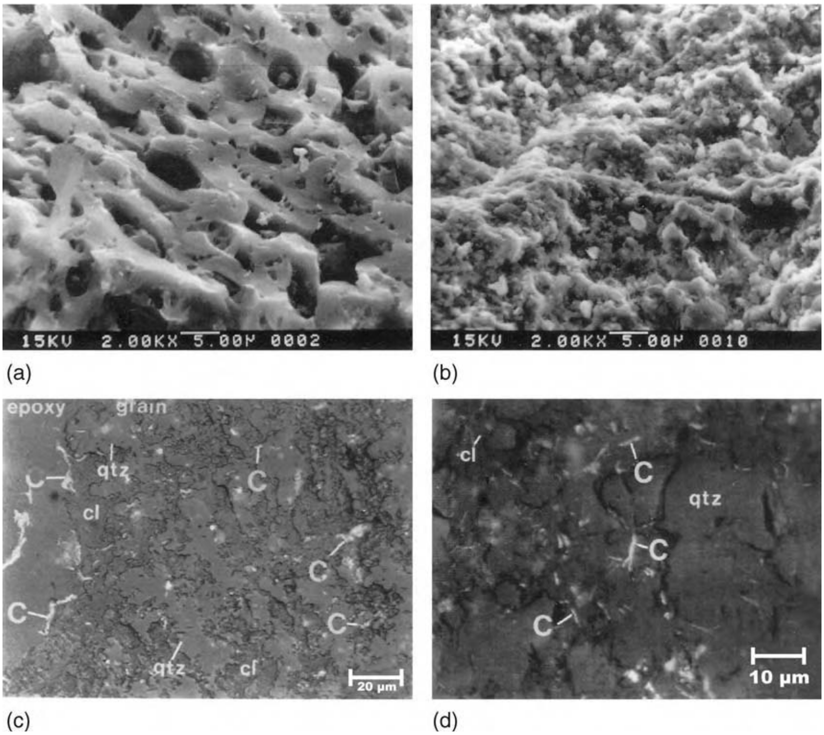


Fig. 15. SEM images of activated carbon (**A**) and carbonaceous matter (**B–D**).

At least in one Carlin-type gold deposit a progressive decrease of surface gold on carbonaceous matter was documented with increasing distance from the orebody. Surface microbeam technology is available for the *in situ* quantification of gold on the surface of mineral particles (see Section 4). Using this technology it is possible to detect and measure gold adsorbed on minerals such as pyrite, kaolinite, illite, micas and chlorites. This gold is sometimes labelled *preg-borrowed* gold given that it is not strongly held up, therefore, potentially recoverable. Preg-borrowing has been observed (in the absence of activated carbon) in the latter part of cyanidation once dissolved gold concentration levels reach a certain threshold level (see Fig. 16).

Cyanicides (Table 6) are species that interfere with gold cyanidation in a number of ways:

- By forming stronger cyanide complexes than gold (*e.g.*, Cu minerals)
- By forming new radicals (*e.g.*, SCN^-)
- By adsorbing CN radicals (*e.g.*, iron sulfides)
- By consuming dissolved oxygen (*e.g.*, pyrrhotite).

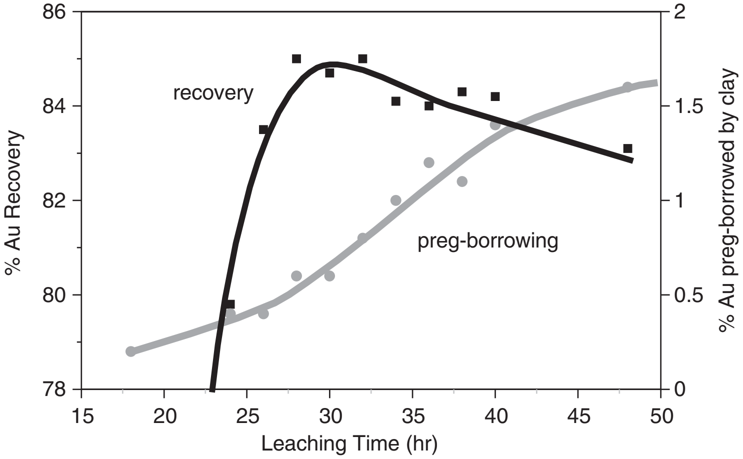


Fig. 16. Effect of preg-borrowing by clays on gold leach kinetics (in the absence of activated carbon).

Table 6
Cyanicides

CN soluble Cu minerals	*Iron sulfides*	*Fe/Sb/As mineral*
$Cu(CN)_x^{y-}$ formation	CN sorption	Dissolved O_2 consumption
Malachite	Pyrite	Pyrrhotite
Azurite		Marcasite
Native Cu		Szomolnokite
Cuprite		Stibnite
Bornite		Gudumundite
Covellite		Berthierite
Chalcocite		Realgar
Tetrahedrite		Orpiment
Elemental sulfur		Arsenopyrite
SCN^- formation		Arsenian pyrite

Early identification of these species is important in order to take the appropriate corrective measures, either in the form of pretreatment options or adjusting operating parameters during leaching to minimize detrimental effects.

2.3.2. Heap leaching

The process mineralogy of gold in heap leach pads has some distinct characteristics that are peculiar to this process as a result of several factors, including the much coarser size range of the material treated, agglomeration, stacking, solution channelling and intermittent solution contact as opposed to complete immersion in tank leaching (see Chapter 19).

The presence of irregular-shaped gold grains (filling fractures or intergranular) in coarser size (>4 mm) ore particles results in overall smaller ratios of exposed to total surface area of the gold grains. Thereby, dissolution is limited to a fraction of the total gold grain surface area. This effect can be further magnified by surface contaminants, which can significantly reduce extraction rates. This phenomenon is manifested by the larger fraction of exposed gold in the coarser fractions from spent heaps. Reduced permeability due to agglomeration, compaction or solution channelling will result in unleached exposed cyanidable gold across all size fractions. Gold grains in the top layer of a heap, because of the greater availability of reagents (cyanide and oxygen) dissolve faster and have less chance of developing a layer of surface contaminants compared to exposed gold from the bottom layer, hence the requirement of properly selecting the leaching/stacking cycles. The presence of water-soluble gold salts in spent heaps, to the point where they can constitute a significant fraction of the unrecovered gold mineralogical budget is the result of intermittent contact with the aqueous solution and hence, poor rinsing and ageing of the spent heap.

2.3.3. Other lixiviants

Environmental concerns and stricter legislation has prompted considerable research on alternative lixiviants, with thiosulfate ($S_2O_3^{2-}$) being the main focus not only because it is a common ingredient in fertilizers but also because of its ability to handle preg-robbing carbonaceous gold ores (see also Chapters 21 and 22). Comparative surface microanalysis of carbonaceous matter from feed and thiosulfate leach tails has revealed that thiosulfate ions can to a large extent remove surface gold from carbonaceous particles. Recoveries of up to 76% of surface gold have been measured. Complete recovery of surface gold from carbonaceous matter is hampered by minor yet measurable sorption of the gold thiosulfate ($Au(S_2O_3)_2^{3-}$) ion.

Of the minor and trace element constituents of native gold grains, mercury has been found at least in one case to interfere with gold dissolution in thiosulfate solution, by developing mercury sulfide (Hg_2S) coatings. There are no surface data available to assess the impact of silver in gold, on the dissolution of the latter. Silver dissolves in thiosulfate solution forming a thiosulfate complex analogous to that of gold, i.e., $Ag(S_2O_3)_2^{3-}$. If the rate of silver dissolution by thiosulfate is slower than that of gold (as in the case of cyanide), then silver will interfere with gold extraction kinetics and most likely result in lower recovery, particularly in the presence of sulfide ions in solution.

Gold thiosulfate has been observed plating on particulates of stainless steel from the grinding media but not on mild steel because of the extensive surface oxidation of the latter.

In systems where gold chloride $AuCl_4^-$ complexes are formed, a fraction was detected partially ($AuCl_2{}^-$) or completely (Au°) reduced on the surface of carbonaceous and pyrite particles, thereby contributing to gold losses.

2.3.4. Response to oxidative pretreatment

Oxidative pretreatment is a requirement for gold ores with a significant fraction of submicroscopic gold in sulfide minerals (referred to as single refractoriness gold ores). Ore mineralogy in general and more specifically the process mineralogy of gold is one of the criteria used for selecting the most appropriate pretreatment option. Carbonate minerals need to be removed prior to pressure oxidation or bioleaching, and this is often achieved in a sulfuric acid pre-oxidation step. Finely disseminated submicron gold-bearing pyrite and arsenopyrite inclusions become liberated in the acid leach step, and hence rendered amenable to cyanidation, unlike inclusions in microcrystalline quartz (*chert*), which remain enclosed and therefore are not accessible for dissolution. Highly preg-robbing carbonaceous submicron gold sulfidic ores (also referred to as ores displaying *double refractoriness*) may need to be roasted to burn the organic carbon, or some other means to minimize preg-robbing. The term *triple refractoriness* is often reserved to describe disseminated siliceous (or *chert*-hosted), carbonaceous sulfidic submicron gold ores.

2.3.5. Process mineralogy of gold from autoclave-CIL circuits

Issues related to mineralogy during pressure oxidation (see Chapter 15) and the ensuing CIL step are listed below:

- Preg-borrowing by residual pyrite, clays and modified micas
- Preg-robbing by carbonaceous matter
- Submicroscopic gold with iron precipitates
- Gold encapsulated by calcium sulfate
- Unreacted locked in *chert* gold-bearing sulfide inclusions.

Gold preg-borrowing by pyrite takes place when conditions in the autoclave favour the formation of gold tetrachloride $AuCl_4^-$ complexes. Chloride ions at concentrations as low as 30 mg/L are sufficient under appropriate pH, Eh and temperature conditions to generate gold tetrachloride, which then is adsorbed and reduced to Au° on pyrite surfaces. Chloride ions may originate from seawater seeping into the orebody (Lihir, Papua New Guinea), from saline ground water, use of magnesium chloride typically used for dust abatement in large open pit mines, from the dissolution of chloride-bearing minerals, or from the reagents added. Under the highly acidic conditions prevailing in the autoclave, gold chloride will also adsorb onto kaolinite and some other clays and micas. This adsorbed gold can easily desorb, hence the term *preg-borrowing*. If there is carbonaceous matter in the ore gold tetrachloride may be preg-robbed. Reclaim water usually contains a few parts per million of free and weak-acid dissociable (WAD) cyanide and in most cases even more thiocyanate (SCN^-) which are enough to dissolve some of the exposed colloidal size gold. Gold cyanide ($Au(CN)_2^-$) and thiocyanate ($Au(SCN)_4^-$) complexes then form and are preg-robbed by carbonaceous matter. Surface microanalysis of carbonaceous before and after acidulation, autoclave discharge and neutralization tanks and from the CIL tails has been used to document and measure preg-robbing as well as to identify the adsorbed gold species (see Fig. 17), thus providing valuable information on the origin of preg-robbed gold for the appropriate remediation action (Fig. 18; Chryssoulis and Dimov, 2004).

Iron hydroxide, arsenate and phosphate precipitated during slurry cooling and neutralization may carry up to one-third of the gold lost in the CIL residue. This gold is submicroscopic with little research done on its origin.

Calcium sulfate mostly in the form of bassanite [$CaSO4\frac{1}{2}H_2O$] and to a lesser extent gypsum [$CaSO_4 \cdot 2H_2O$] forms in the neutralization tank. It does encapsulate gold relinquished during pressure oxidation thus preventing extraction and may account for up to 20% of the gold in the CIL residue. Unreacted gold-rich pyrite microinclusions locked in *chert* comprise the hardest to extract form of gold from Carlin-type ores and sets a practical minimum for CIL tails grade. A gold deportment in an AC/CIL tails sample is depicted in Fig. 19.

2.3.6. Process mineralogy of gold from roaster-CIL circuits

Mineralogical factors that usually have an impact on gold extraction from carbonaceous ores by the roasting/CIL process (see Chapters 17 and 18) are listed below:

- Unoxidized locked in rock mineral particles gold-bearing sulfide inclusions
- Unleached oxidized gold-bearing sulfide (FeO_x) inclusions in rock mineral particles
- Formation of gold-bearing ferrous pyroarsenite
- Entrapment by glazing of porous FeO_x particles
- Submicroscopic gold with iron precipitates
- Preg-robbing by unburnt carbonaceous matter
- Gold encapsulated by calcium sulfate.

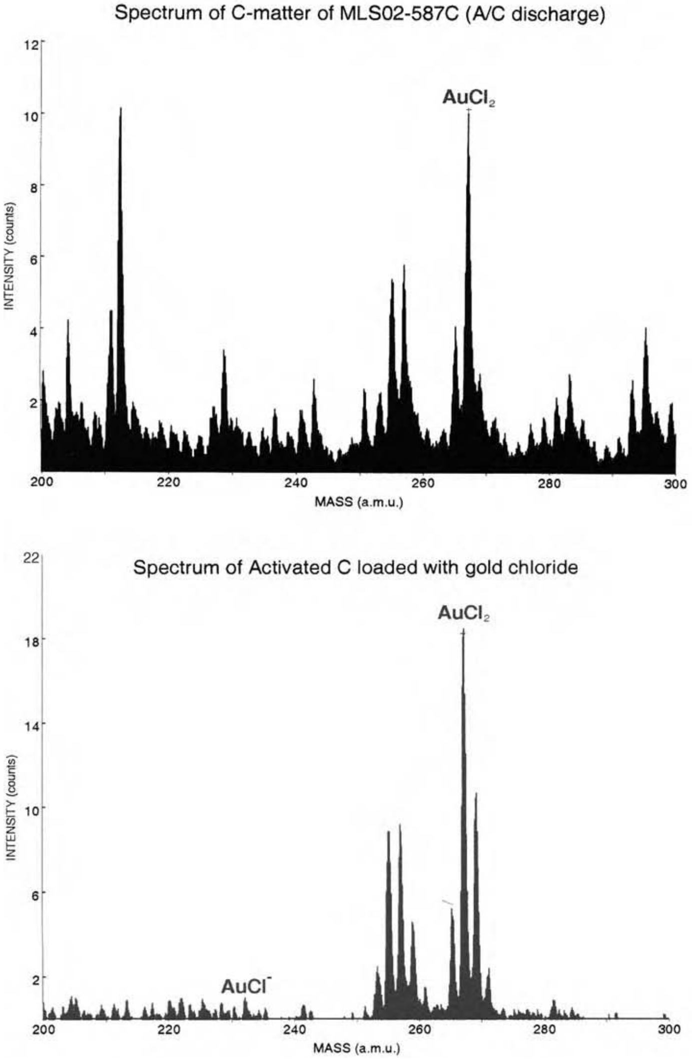


Fig. 17. Speciation of gold adsorbed on carbonaceous matter of AC/CIL tails. TOF-LIMS surface spectra of carbonaceous matter from AC discharge sample (to) and of activated carbon contacted with gold tetrachloride ($AuCl_4^-$) solution. In both cases the dominant gold species observed are atomic gold (Au°), which is not shown and gold dichloride ($AuCl_2^-$).

Additional issues identified by investigating tails of older single-stage roaster/CIL circuits (Gold Giant, Con, NWT, Canada) are:

- Partially roasted free sulfide particles
- Low-permeability calcine particles.

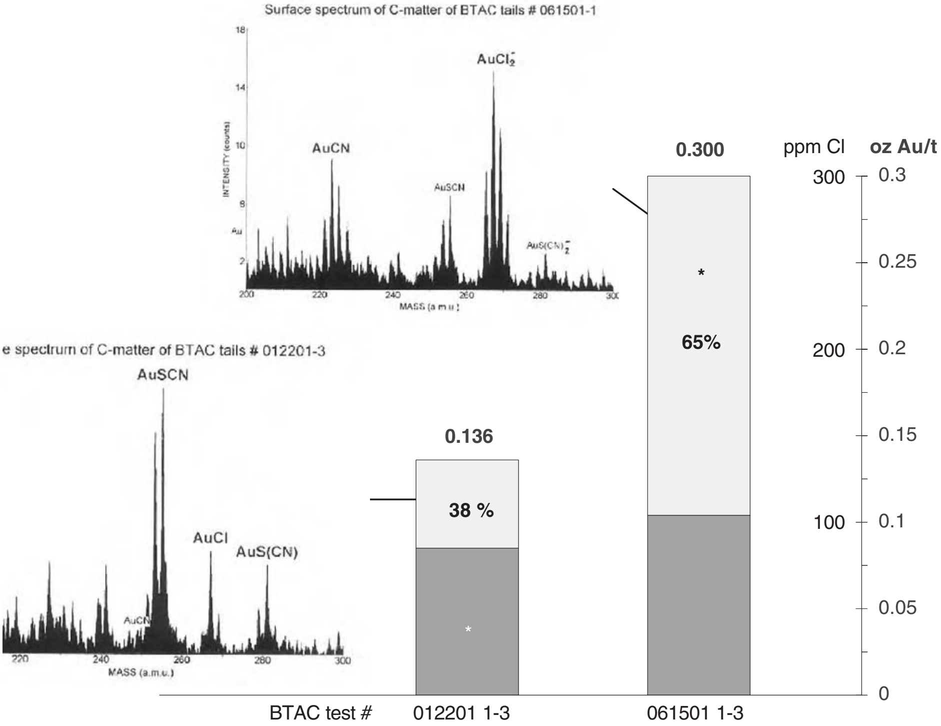
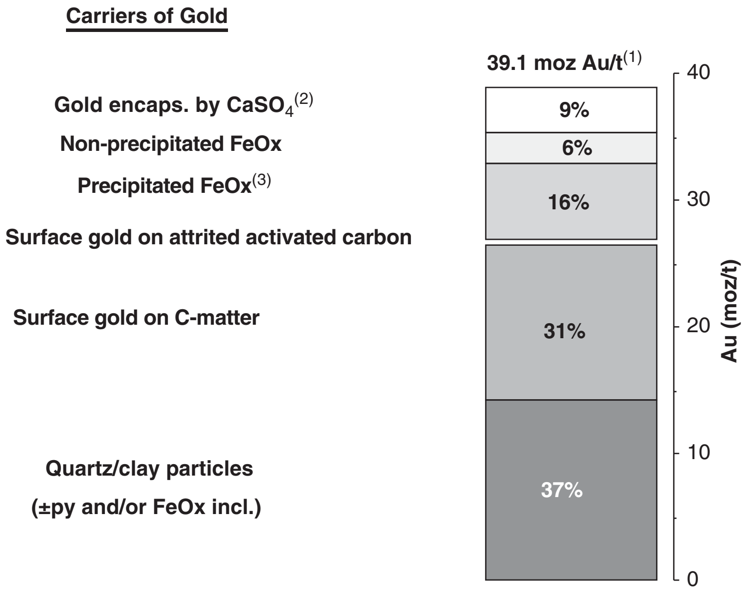


Fig. 18. Quantification and speciation of gold adsorbed on carbonaceous matter of AC/CIL tails. At 300 mg/L Cl^-, the dominant adsorbed gold species is gold dichloride, which accounts for 65% of the residue grade. At 130 mg/L Cl^-, the dominant adsorbed gold species is a derivative of gold thiocyanate: $AuS(CN_2)^-$.

Partially roasted free sulfide particles have been found to be present in single-stage roaster calcine, but are not typically observed in two-stage roaster calcine. Partially roasted free pyrite particles display concentric rimmings of hematite [Fe_2O_3], maghemite [Fe_2O_3 with up to 8% FeO] and magnetite [Fe_3O_4] with a pyrite core, as shown in Figs. 20 and 21 and Plates 7–9. The core of partially oxidized arsenopyrite particles is a gold-bearing pyrrhotite (Chryssoulis, 1991). The submicroscopic gold content of the pyrrhotite is comparable to that of the precursor arsenopyrite (see Fig. 22), indicating that arsenic was removed leaving behind the gold. Low-permeability hematite/magnetite particles are characterized by well-developed concentric pores and minor radiating pores, yielding inferior permeability despite the high porosity of the particle. Good permeability of calcine particles is a key requirement in order to be able to leach out colloidal size (<1 μm) gold inclusions formed during roasting.



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(1) mineralogically accounted for 40.2moz Au/t
(2) including calcium orthoarsenate
(3) including Fe oxyhydroxides, arsenates, phosphates

Fig. 19. Gold deportment in AC/CIL tails. The height of the bar is proportional to the tails grade, while each segment shows the fraction of gold contained in each carrier.

Glazing, also referred to as *sintering* of the surface layer of porous hematite particles, is the result of a higher roasting temperature or longer residence time. It does reduce permeability of the particle by sealing pores on the surface and thereby porous particles with a glazing typically have a higher gold content (see Fig. 23).

Maghemite, which essentially is hematite with magnetic properties, is an intermediate product of magnetite to hematite oxidation during roasting. It usually carries marginally more gold than the porous hematite particles, presumably because of its visibly lower porosity. The gold content of maghemite particles increases significantly when maghemite is intergrown with ferrous pyroarsenite [Fe_2AsO_5]. The presence of this compound has been documented in calcines produced from high in arsenic roaster feeds. Gold in ferrous pyroarsenite is usually either in solid solution or as very fine (<0.05 nm) colloidal gold.

As with leached autoclave residues there will always be some gold associated with precipitated iron hydroxyl-oxides and cyanidable gold that has been encapsulated by calcium sulfate; however, it is typically present in lower absolute (g/t) and relative (%) concentration.

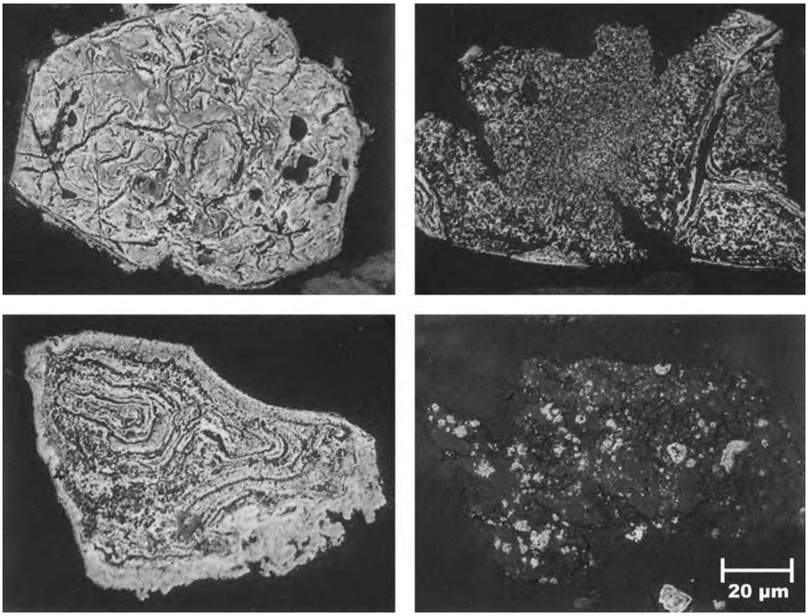


Fig. 20. Morphological types of roaster calcine particles (left to right): maghemite, porous hematite, rimmed (glazed) porous hematite and disseminated (in rock hematite).

Roasters are very efficient at burning carbonaceous matter, but 100% burning efficiency is rarely achieved. Therefore, residual exposed carbonaceous matter can become very active as a result of the roasting process. Such carbonaceous particles are fully loaded with gold, as documented by surface microbeam analysis (Fig. 24) and contribute to gold losses in leached roaster calcines. Speciation of adsorbed gold has identified metallic gold (Au°), gold cyanide ($Au(CN)_2^-$) and thiocyanate ($Au(SCN)_2^-$). Traces of cyanide and thiocyanate in the reclaim water complex the readily soluble colloidal gold produced in the roaster, thereby leading to possible preg-robbing ahead of the CIL circuit.

In the coarse-grained (>100 μm) microcrystalline quartz (but also other rock mineral) particles with finely disseminated tiny (1–2 μm) gold-rich pyrite inclusions, the inclusions towards the perimeter of the particles are oxidized (as clearly indicated by their conversion into hematite); however, pyrite inclusions in the core area in some instances remain unoxidized. This is not observed in particles finer than ~53 μm. What is more important is that the gold content of rock mineral particles with hematite inclusions is only slightly lower than that of the rock particles with pyrite inclusions indicating that the "released" gold could not be removed, most likely due to lack of sufficient accessibility by the cyanide solution. This form of gold sets the minimum attainable grade for the leached calcine.

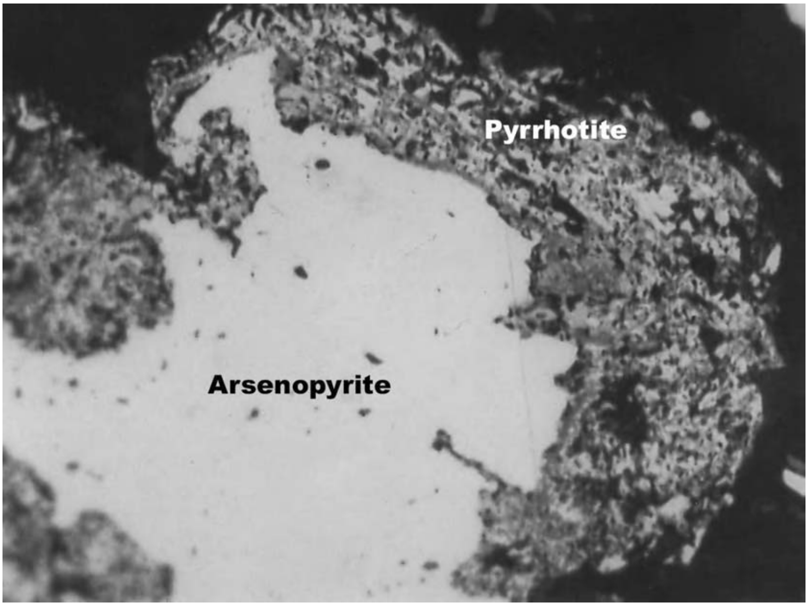


Fig. 21. Reaction rims of roaster calcine arsenopyrite. The core is arsenopyrite [FeAsS], the inner rim is a gold-bearing pyrrhotite [$Fe_{(1-x)}S$] and the outer rim is porous hematite [Fe_2O_3]. Therefore, dearsenification takes place first [(Fe,Au)AsS → (Fe,As)S] then desulfurization [$(Fe,Au)S \rightarrow FeO_x(Au)$], with colloidal gold forming in the second step (Con mine, NWT, Canada).

2.3.7. Process mineralogy of gold from bio-oxidized leach circuits

Mineralogical examination of pyrite, arsenopyrite [FeAsS] and loellingite [$FeAs_2$] crystals before and after bio-oxidation in the laboratory, using a *Thiobacillus ferrooxidans* with minor *Leptospirillum ferrooxidans* bacterial culture, revealed that bacteria attached preferentially to the more arsenic-rich mineral in the assemblage (*e.g.*, arsenopyrite over pyrite and loellingite over arsenopyrite) and secondly to the more arsenic-rich zones or domains in compositionally inhomogeneous crystals (see Chapter 16 for more detail on bio-oxidation of gold ores). Given the preferential association of submicroscopic gold with arsenic in both the pyrite and arsenopyrite, this coincides with preferential bio-oxidation of gold-rich zones or domains (see Fig. 25). Apart from compositional variation, defects in the crystal structure of the host sulfide also increase the rate of bio-oxidation (Claassen, 1993). Five-fold increases in the rate of oxidation were noticed between arsenic-rich and arsenic-poor zones of arsenopyrite and between arsenopyrite and the arsenic-rich zones of pyrite (3.6% (m/m) As) from the Sheba mine (Claassen, 1993). Comparative surface microanalysis of sulfide particles before and after

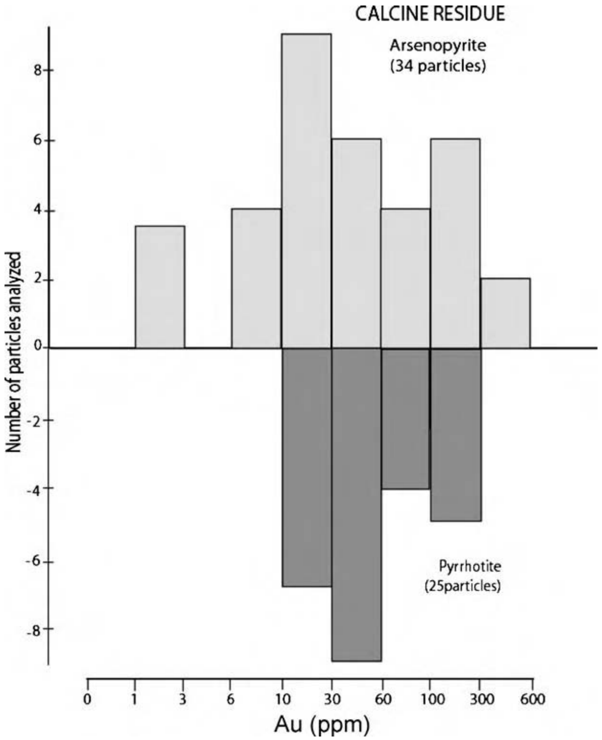


Fig. 22. Submicroscopic gold concentration (in ppm) of arsenopyrite and roaster calcine pyrrhotite formed by the release of arsenic ($FeAsS + \frac{3}{2}O_2 \rightarrow FeS + \frac{1}{2}As_2O_3\uparrow$).

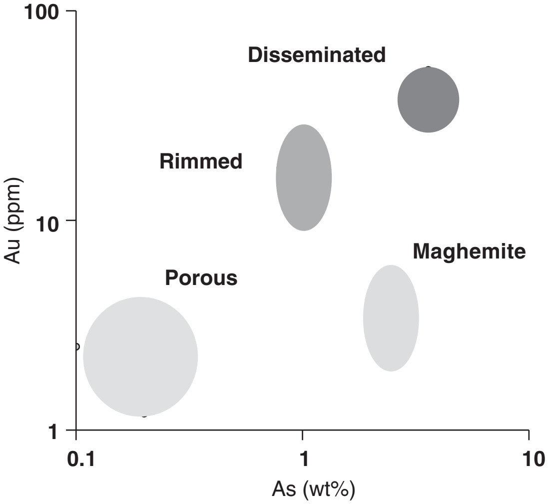


Fig. 23. Average gold and arsenic content of different types of calcine particles. *Rimming* (or *glazing*) of porous particles reduces permeability, sealing off cyanidable gold.

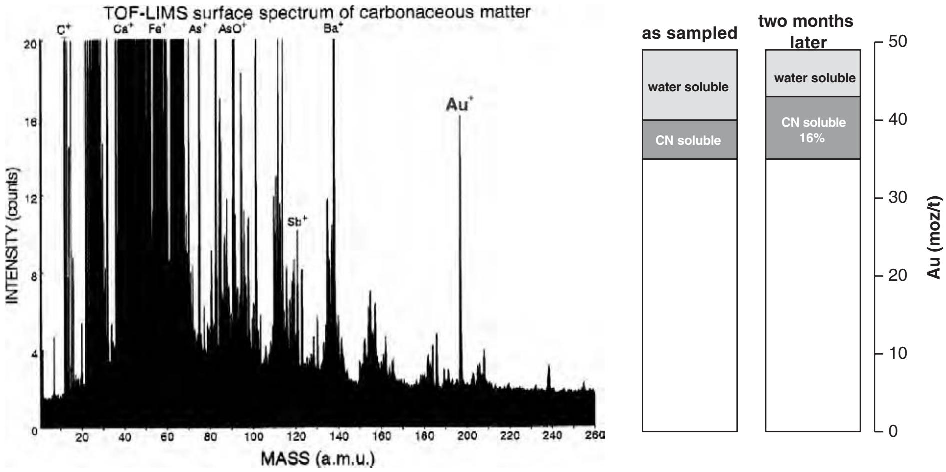


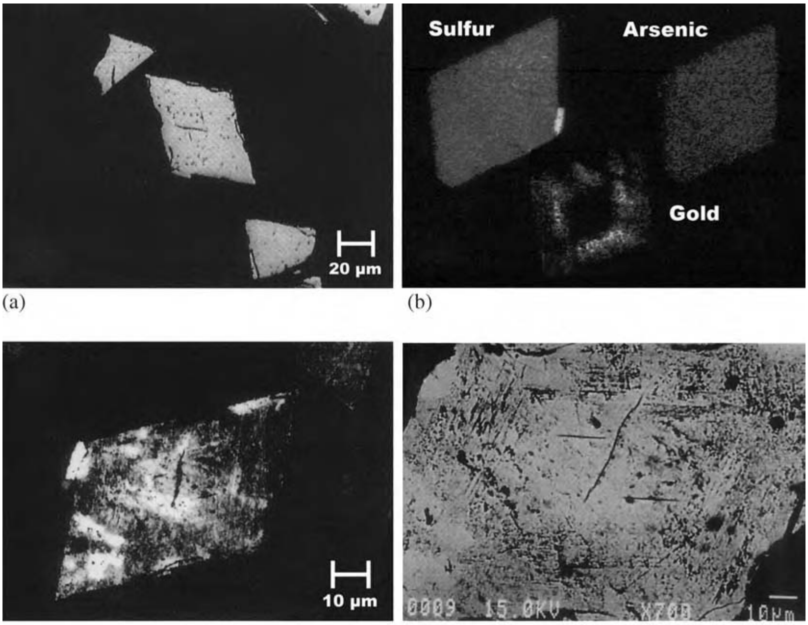
Fig. 24. Surface gold on unburned carbonaceous matter of a roaster/CIL tails sample analysed soon after sampling and 2 months later. The change from water-soluble to cyanide-soluble gold indicates *metallization* of surface gold, originally present in water-soluble form.

bio-oxidation showed a major increase in the surface gold concentration after bio-oxidation (see Fig. 26), an independent confirmation of freeing up submicroscopic gold tied up in the sulfide structure (Agha *et al.*, 1998).

Gold encapsulated by elemental sulfur produced during bio-oxidation and gypsum produced during neutralization are potential causes of increasing gold losses. The presence of elemental sulfur also leads to somewhat higher cyanide consumption due to thiocyanate formation.

2.3.8. *Response to ultrafine grinding CIL*

UFG of pyrite concentrates for subsequent leaching is used in ores, where refractoriness to direct cyanidation arises from fine to ultrafine (<20, $>0.02\,\mu m$) gold mineral inclusions in the pyrite and/or arsenopyrite. By grinding to 80% passing $10\,\mu m$ a significant fraction of the colloidal size ($<0.5\,\mu m$) gold is also being exposed and rendered amenable to cyanidation. On the downside, the huge increase in surface area of pyrite that is created by UFG magnifies 10-fold any preg-borrowing effects, probably assisted by free cyanide, consumption by adsorption onto pyrite surfaces and the formation of thiocyanate (SCN^-). If there is carbonaceous matter in the UFG concentrate to be leached, it can contribute to significant losses, because of its relatively huge surface and the irreversible sorption of gold (preg-robbing). More details on this technique may be found in Chapter 12.



(a) (b)

(c) (d)

Fig. 25. Preferential bio-oxidation of gold-rich zones in arsenopyrite [FeAsS].

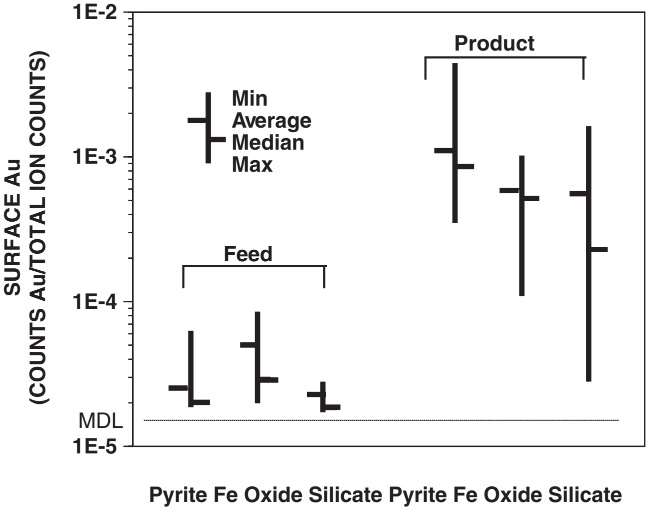


Fig. 26. Surface gold on various mineral particles from the Harbour Lights (Australia) feed and unleached bio-oxidation product. Note the major increase in surface gold in the bio-oxidation product.

3. METHODOLOGY FOR STUDYING GOLD MINERALS

Gold minerals are few, with somewhat unique properties (high specific gravity, brightness and average atomic number) making it relatively easy to pre-concentrate them for characterization and the identification under the optical and electron microscopes. For quantitative gold deportment investigations, it is important to remember the different forms of gold, measure each gold form independently and make sure limitations of the measuring method/device do not compromise results, or at least be aware of that possibility.

Diagnostic leaching (Tumily *et al.*, 1987; Lorenzen, 1995), the first method for complete gold disposition evaluations, was warmly embraced by industry and metallurgical laboratories because of its simplicity, speed, need for specialized instrumentation and relatively low cost. It consists of a series of cyanidation steps in between a series of progressively more aggressive acid-digestion steps. Thus, it apportions a gold assay into water-soluble, cyanidable-exposed gold, and gold enclosed in carbonates, in sulfides and in silicates (see also Chapter 4)

Gravity-recoverable gold (GRG) tests at three successively finer grinds coupled with automated image analysis (AIA) search for gold minerals in each of the three gravity concentrates and the gravity tails (Guerney *et al.*, 2003) and provides information on the gravity-recoverable gold at different grind finenesses, the gold grain size distribution, as well as their association and composition.

Gravity concentration using heavy media, screening of the *heavy mineral* fraction followed by microscopist-assisted or automated search for gold minerals and assaying of the *light* fraction (Zhou *et al.*, 2004) is a variant of the GRG approach. In this method gold is differentiated into: free, visible gold associated with sulfide minerals and the heavier rock/sulfide binaries; and gold associated with rock and light binaries.

Gold deportments address all forms of gold as part of the same procedure. Unlike the other methods, each form is independently assessed (not by difference unlike the other methods) and where possible are confirmed using a complementary method. Special care is exercised to not miss important fractions of gold, such as free gold in the slimes fraction. Different deportment procedures have been developed to address the specifics of different gold beneficiation processes. Thus, the term gold *carriers* has been introduced to better characterize gold losses in flotation tails. A typical example of classification of unfloated gold would be: free gold of floatable size classes (<100, $>5\,\mu m$), free gold in the slimes ($<5\,\mu m$), gold associated with valuable sulfides, with pyrite, with middlings and with rock mineral particles; submicroscopic gold in pyrite and arsenopyrite (see Fig. 27). The latter determination includes, when required, differentiation between solid-solution

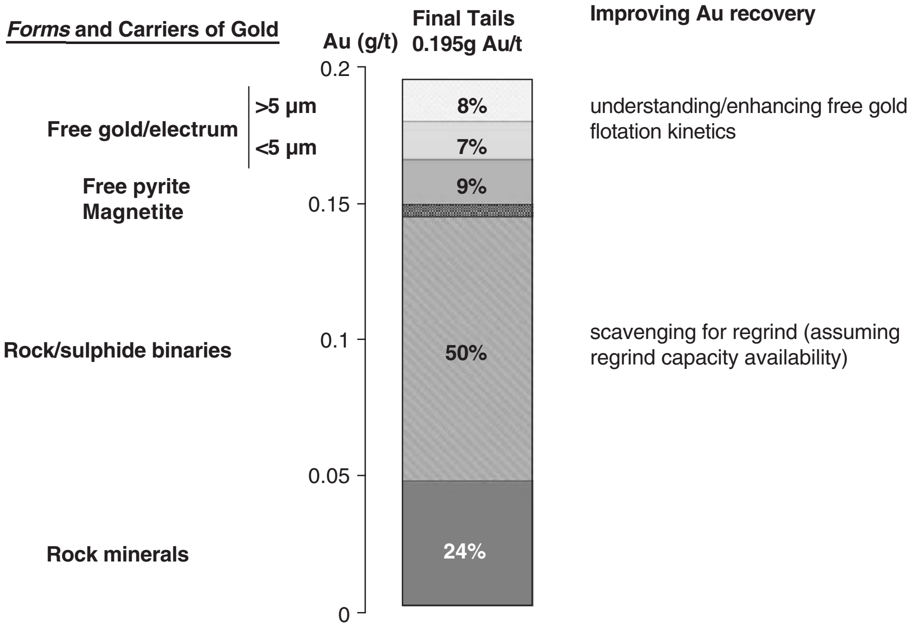


Fig. 27. Typical graphic illustration of gold disposition in flotation tails, tailored as required to address specific issues.

and colloidal-size (<0.5 μm) particulate gold (which is pertinent to a UFG/CIL follow-up treatment of the concentrate) and the measurement of any significant variation in submicron gold concentration between the pyrite and arsenopyrite morphological types, which can exhibit very different degrees of liberation in grinding and respond differently to flotation. Good examples are the high/low arsenic and gold pyrites of Olympias (Greece) and the numerous Carlin-type ores.

Additional characterization includes the size distribution of the associated gold minerals and determining if there is a specific target grind for liberation, as well as the identification of surface contaminants, which hampered recovery of free gold of floatable size classes. A more recent tool to help find ways to augment the recovery of free gold is the matching of a secondary collector to the rejected gold grain composition (Chryssoulis *et al.*, 2003a).

In the case of leach tails the following types of gold are used to characterize the unleached gold: water-soluble gold salts; free and exposed cyanidable gold; enclosed cyanidable gold (including determination of a target grind to expose such gold); submicroscopic gold in sulfides and surface gold on carbonaceous matter. If the sample has a high pyrite or clay mineral content then surface gold is measured on both. Surface contaminants interfering with gold extraction are determined directly by analyzing the surfaces of residual

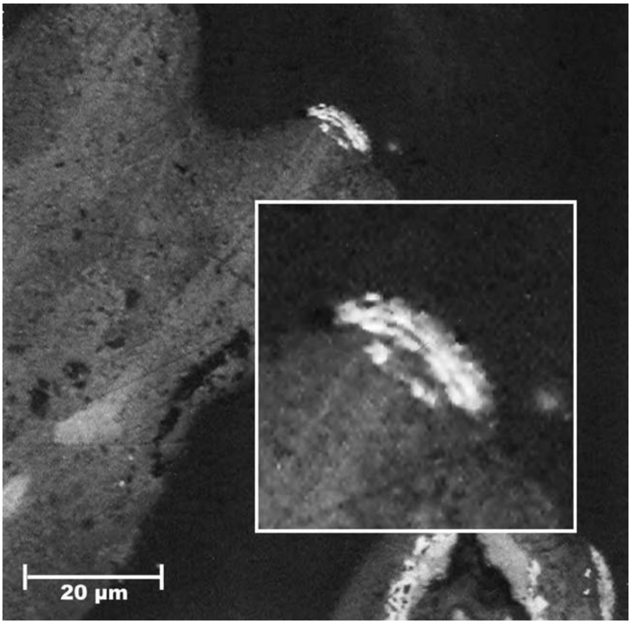


Fig. 28. Gold plating on completely oxidized high-chrome steel from the grinding media. Inset: high resolution SEM image of plated gold showing concentric growth bands. Sample collected from Neutralization Tank No. 1. Gold plates selectively on areas where a chromium sulfate salt is more abundant.

free gold grains. Speciation of surface gold on carbonaceous matter provides valuable information on the mechanism of gold dissolution and the source of the unwanted gold ligand.

In the case of pre-oxidized samples the following additional carriers of unrecovered gold are evaluated: gold encapsulated by calcium sulfate (and for certain processes elemental sulfur), gold in precipitated iron hydroxyl-oxides and on oxidized portions of grinding media (see Fig. 28), as well as gold in roaster calcine particles of distinct morphological and compositional type.

The gold deportment procedure was developed to provide a clear and accurate picture of the disposition of the unrecovered gold in tailing samples, provide a ranking of the causes for the observed losses, identify the means for augmenting recovery and set a realistic target for the tails grade. An abbreviated version is used for studying gold deportments in feed samples to predict metallurgical behaviour.

Given the low grade of the tailings, large samples (1–100 kg, depending on gold assay) are used, with particular attention paid to characterizing gold in the slimes fraction. This provides accurate assessments of free gold losses within and below optimum floatable size classes. The main drawbacks of gold deportment studies is that they are time consuming, involving several steps and a number of microprobe techniques. These are discussed in the next section.

4. INSTRUMENTAL ANALYSIS FOR GOLD

A variety of methods are available for assessing gold grain size distribution, liberation and exposure of gold minerals, with AIA techniques having gained broad acceptance over the last two decades (Lastra *et al.*, 1998). AIA methods rely on X-ray dot maps or back-scattered electron images (BSE) produced by the SEM or electron-probe microanalyser (EPMA). Sophisticated automated search protocols for gold minerals have been developed but can be at a disadvantage to the trained eye of the ore microscopist in terms of speed. The scarcity of gold mineral grains in low-grade samples such as tailings, coupled with the strong partitioning of submicroscopic gold to certain morphological types of pyrite, in the case of refractory gold ores, remain the two main disadvantages of AIA. The practical limit of detection for gold grains is 1–2 μm defined by the step size in the AIA scanning grid. The best way to evaluate gold grain *flakiness* is still the stereomicroscope that provides 3D vision, the alternative being measurement of aspect ratios (longest/shortest diameter) by 2D image analysis. Gold minerals are usually identified by reflected light microscopy, while their composition is determined by EPMA.

SIMS is superior to any other microbeam technique for determining submicroscopic gold because of its accuracy (provided by matching mineral standards; Chryssoulis *et al.*, 1987), sensitivity, covering the entire range of gold concentration from 0.2 ppm up to a couple of percent; and its ability to differentiate between solid solution and colloidal size (0.02–0.5 μm) particulate gold (Fig. 29; Plate 6). SIMS analyses successively deeper layers with time. No other microbeam technique has all these attributes.

HR-TEM is used to detect, identify and measure colloidal-size gold nanoinclusions. Gold inclusions as small as 50 nm (= 0.05 μm) have been imaged (see Fig. 30) by HR-TEM (Bakken *et al.*, 1989).

Micro-PIXE (particle-induced X-ray emission) has been used to measure submicroscopic gold concentrations in sulfide minerals (Cabri *et al.*, 1991) as well as image concentration distributions (Ryan, 2001). It is not the preferred choice for sub-micron gold microanalysis because the limit of detection is rather high (~25 ppm) due to interference from arsenic, the large analytical microvolume (5,000 μm^3) and because it does not have the capability to differentiate between micrometer size gold inclusions and solid-solution gold.

X-ray photoelectron spectroscopy (XPS) and X-ray absorption near-edge structure (XANES) spectroscopy are the two techniques used to determine

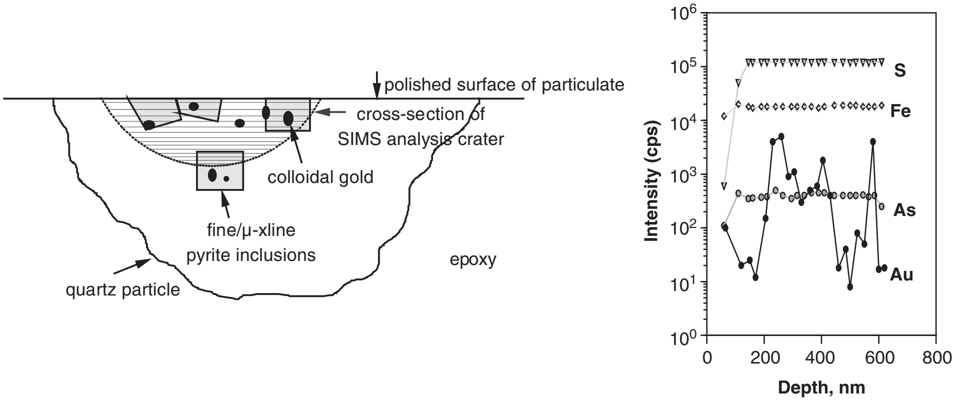


Fig. 29. Schematic cross-section of SIMS analysis of a gangue mineral particle containing microcrystalline pyrite and colloidal-size gold (vertical-scale grossing exaggerated) and SIMS depth profile (right).

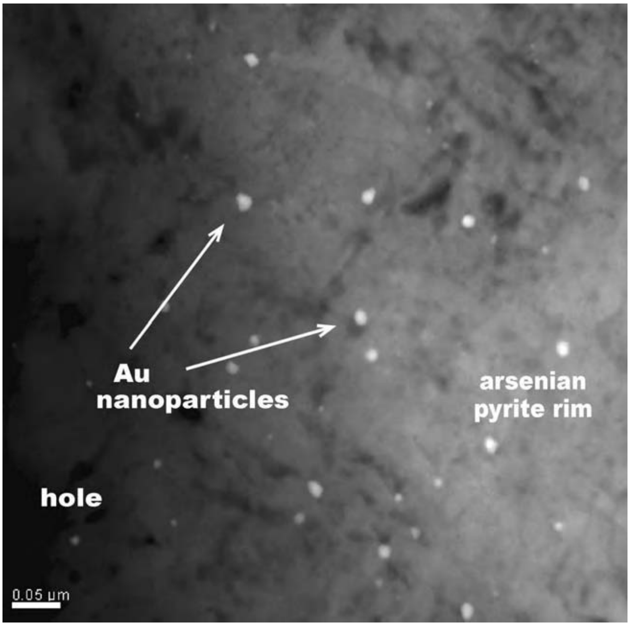


Fig. 30. HR-TEM image of colloidal-size gold inclusions in arsenian pyrite (courtesy of Martin Reich).

the chemical state of gold in the crystal structure of arsenopyrite (Cabri *et al.*, 2000) and pyrite (Simon *et al.*, 1999). XPS was also used to confirm the identity of gold species adsorbed onto activated carbon (Dimov *et al.*, 2003).

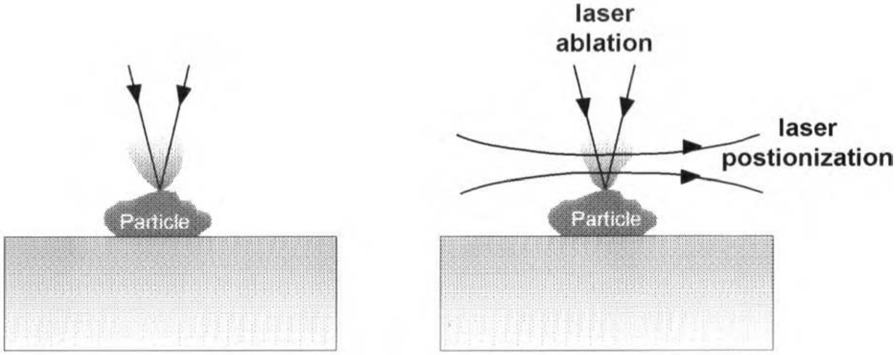


Fig. 31. Schematic cross-section of TOF-LIMS analysis. Unlike microbeam techniques for bulk microanalysis of mineral particles (Table 5), which use polished grain mounts, surface techniques analyse rough particles, appropriately arranged (in lines or clusters) on a conductive substrate (typically indium foil).

Time-of-flight laser-ionization mass spectrometry (TOF-LIMS) is ideal for inorganic surface microanalysis of gold particles (Fig. 31) because of its combined superior surface sensitivity (sampling depth 0.01–0.03 μm) and analytical sensitivity (<10 ppm in the surface layer being analysed); the small adjustable analytical spot size (2–30 μm); its capacity to differentiate surface from subsurface species by repeating the analysis on the same spot; its easy to interpret spectra; but most importantly the speed of analysis, which makes possible for large data sets to be collected for comparative statistical analysis (Chryssoulis *et al.*, 1992). TOF-LIMS is used also for the identification (Fig. 17) and quantification of gold species adsorbed on carbonaceous matter (Chryssoulis and Dimov, 2004).

Time-of-flight resonant ionization mass spectrometry (TOF-RIMS) differs from TOF-LIMS in that the wavelength of the ionizing laser is pre-selected so as to selectively ionize the element of interest, in this case gold. Using this approach a minimum detection limit of 0.01 ppm for Au is achievable. TOF-RIMS has all the attributes of the TOF-LIMS technique but is not as fast (Dimov *et al.*, 2002).

Laser inductively coupled plasma mass spectrometry (L-ICP-MS) although it can have subpart per million sensitivity, it suffers from a very large microanalytical volume (Fig. 32) and at present has limited applicability in gold deportment investigation.

Time-of-flight secondary-ion mass spectrometry (TOF-SIMS) is more suitable for organic surface microanalysis, after choosing carefully operating conditions to preserve molecular ions (see Chryssoulis *et al.*, 1995). Collector molecules can be identified from the unfragmented molecular ions (Fig. 33) and loadings measured by sizing the parent peak against a series of standards

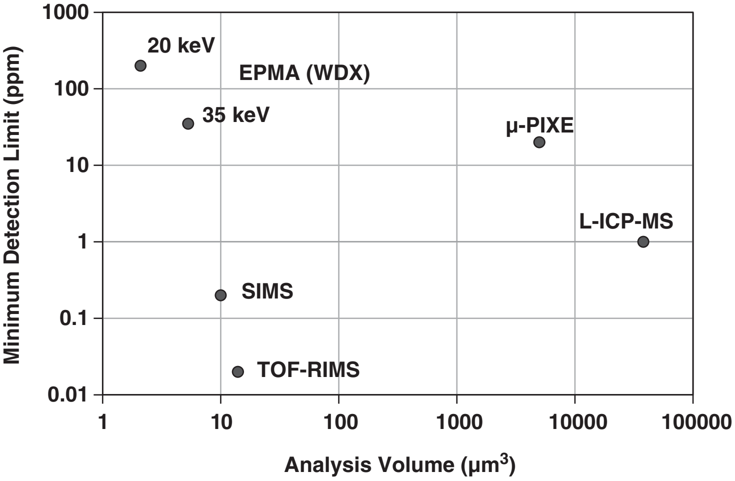


Fig. 32. Microbeam techniques for bulk microanalysis of gold in pyrite. Techniques with large analytical volumes cannot differentiate between solid-solution and colloidal size particulate gold, which is important in UFG/CIL.

(Chryssoulis *et al.*, 2003a). With vacuum ultra-violet (VUV)-TOF-LIMS there is even less fragmentation of the collector molecule, so it is by an order of magnitude more sensitive than TOF-SIMS for cationic collectors (Dimov and Chryssoulis, 2004). Table 7 lists all microbeam techniques used for gold analysis depending on the target area: surface vs. bulk of the particle.

5. CONCLUDING REMARKS

Characterization of gold minerals and carriers in composite ore sample can be used to diagnose and predict metallurgical response, identify potential problems and help in the design of a more robust metallurgical testwork program. The deportment study should be quantitative; however, it does not require the detail of gold deportments for tailings. Modal gold analysis of all fractions including the slimes, coupled with an overall mineralogical study is usually adequate. It is important to carry out the gold mineralogical investigation on all major ore types, to predict variation in metallurgical response as well as establish its cause.

Detailed gold deportment study of tailing samples with the assistance of all available microbeam techniques is used to determine each form and carrier of gold on a quantitative and independent basis to assess unequivocally and to rank causes for not recovering gold. This is perhaps the best approach for identifying problems in gold plants, for setting realistic targets for tails grade and assisting in developing strategies for pushing recovery even higher.

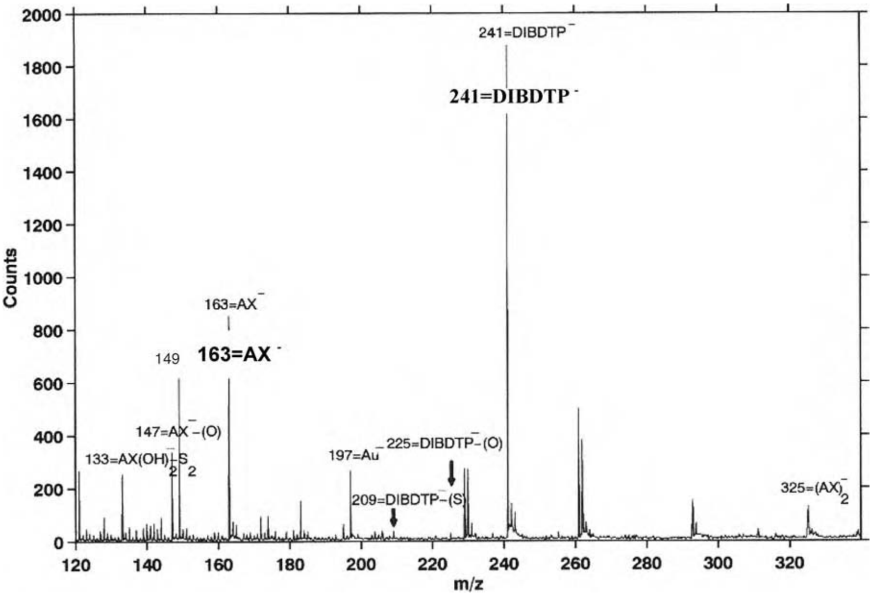


Fig. 33. TOF-SIMS spectrum of gold particle loaded with DIBDTP and amyl xanthate. The spectrum is dominated by the unfragmented collector molecular ions (AX^- at 163 m/z and $DIBDTP^-$ at 261 m/z).

Table 7
Microbeam techniques for bulk and surface microanalysis of mineral grains

Bulk analysis	Surface analysis
EPMA (EDX/WDX)	TOF-LIMS
μ-PIXE	TOF-SIMS
SIMS	VUV-TOF-LIMS
TOF-RIMS	SALI
L-ICP-MS	TOF-RIMS
Modal analysis (mineral abundance and association)	
AIA	

EPMA, electron-probe microanalysis; EDX, energy-dispersive X-ray analysis; WDX, wavelength-dispersive X-ray analysis; μ-PIXE, micro-particle-induced X-ray emission; SIMS, secondary-ion mass spectrometry; TOF-LIMS, time-of-flight laser-ionization mass spectrometry; TOF-RIMS, TOF resonant-ionization mass spectrometry; VUV-TOF-LIMS, vacuum ultraviolet TOF-LIMS; SALI, surface analysis by laser ionization; AIA, automated image-analysis.

Partial (narrow scope) gold deportment studies of intermediate products have been used to understand the kinetics and efficiencies of the gold unit process (*e.g.*, flotation, leaching, pressure oxidation and bioleaching). Gold deportment in final flotation concentrates is carried out in conjunction with the study of cleaner (scavenger) tails to assess the potential for improving rejection of insolubles or pyrite, without sacrificing gold recovery.

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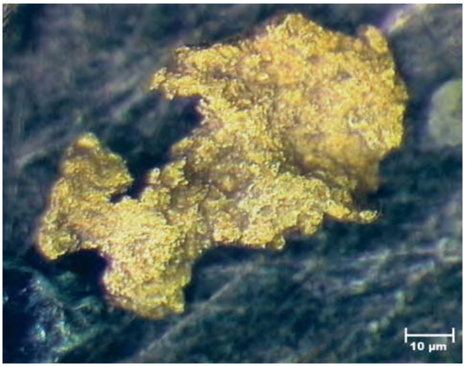

Plate 1. Coarse gold flake from flotation final tails.

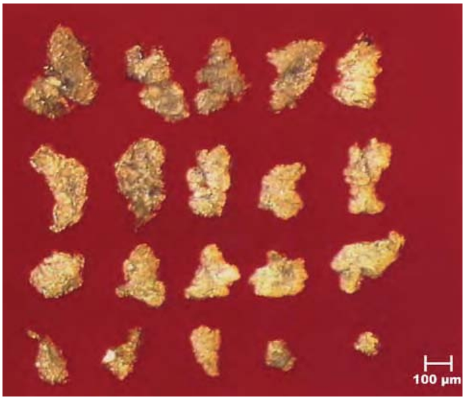

Plate 2. Coarse gold flakes from column cleaner tails.

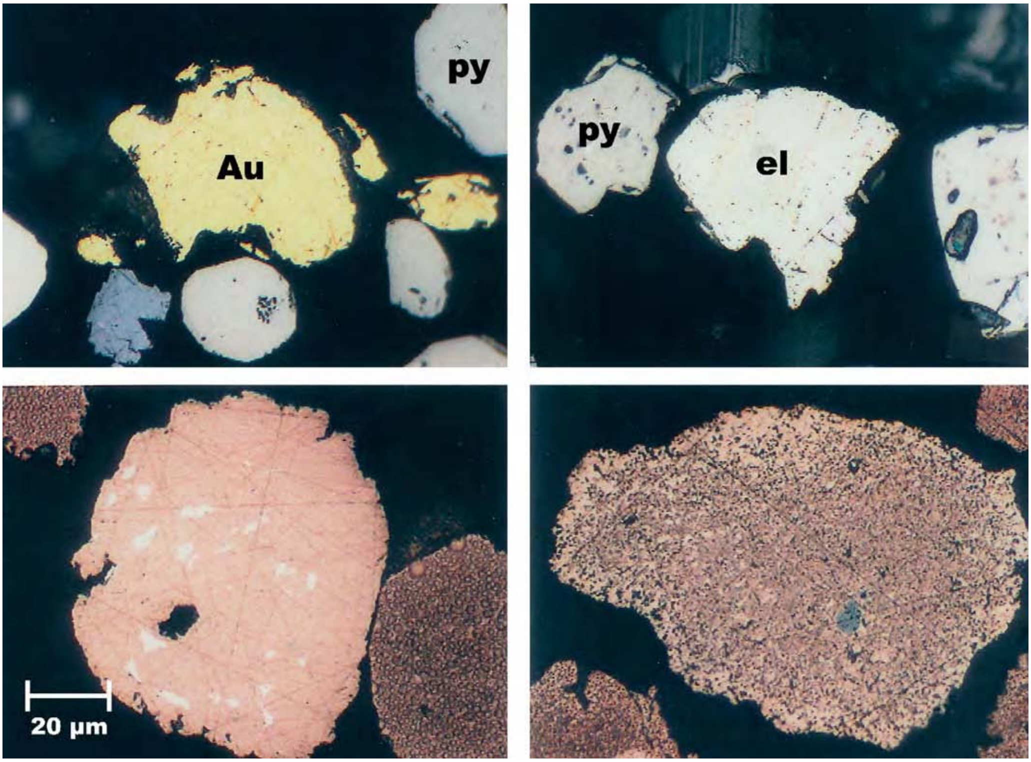

Plate 3. Gold minerals (clockwise): native gold, electrum, auricupride [Cu_3Au] (with native silver inclusions) and tetrauricupride [AuCu].

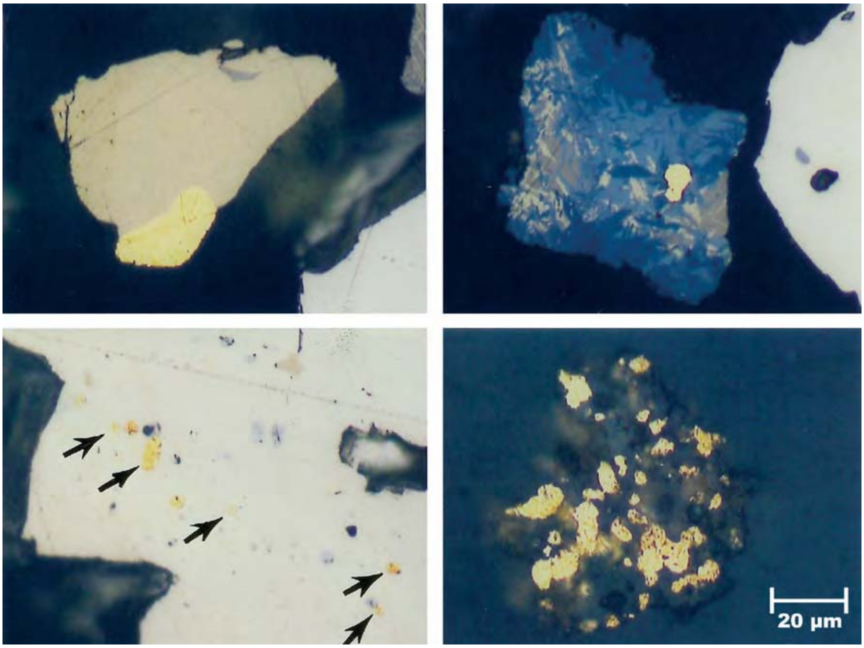

Plate 4. Gold mineral associations (clockwise): native gold rimmed by electrum [Au,Ag], native gold attached to chalcopyrite [$CuFeS_2$], enclosed in pyrite [FeS_2] and quartz (the latter two are considered in most cases as unfavourable associations).

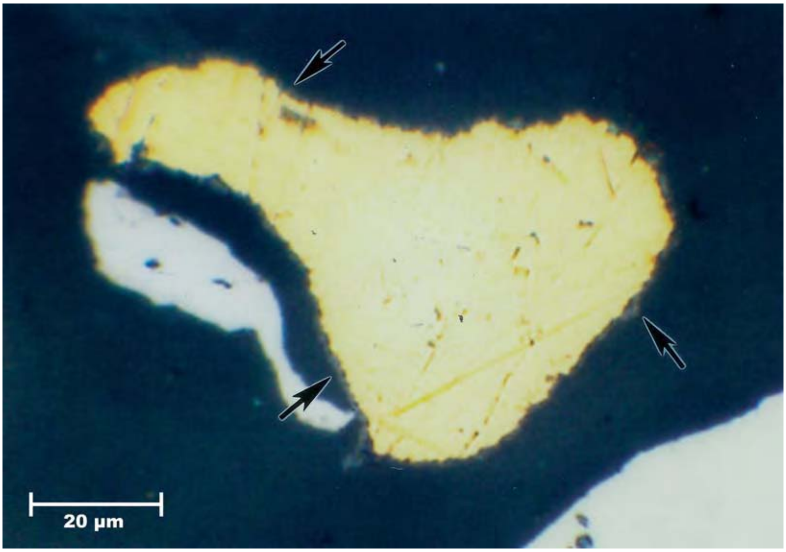

Plate 5. Silver arsenate coating on residual free gold particle; in most cases the coating is too thin to be seen under the microscope; however, it is readily detectable by laser-probe microanalysis (TOF-LIMS).

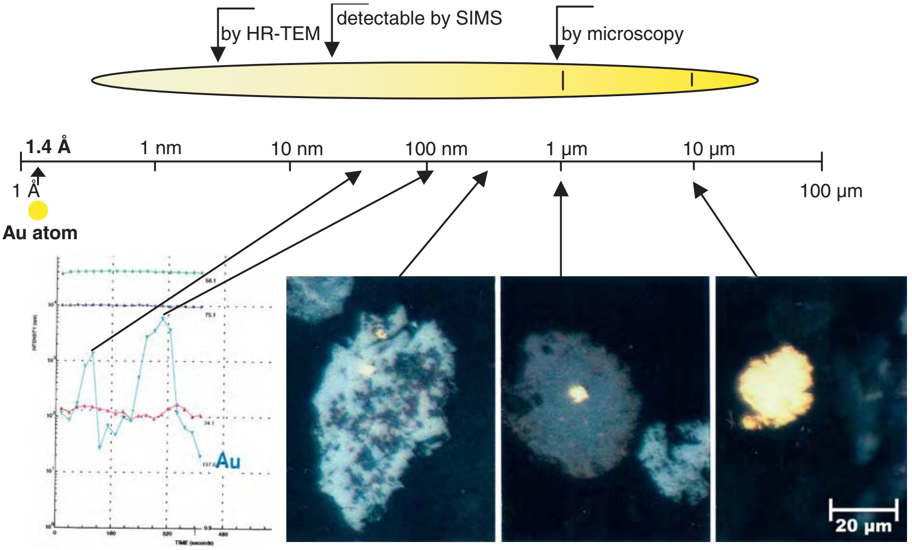

Plate 6. Continuum between solid solution, colloidal and micrometre-sized gold with method of detection. Gold inclusions are hosted in hematite [Fe_2O_3] and goethite [$FeO \cdot OH$].

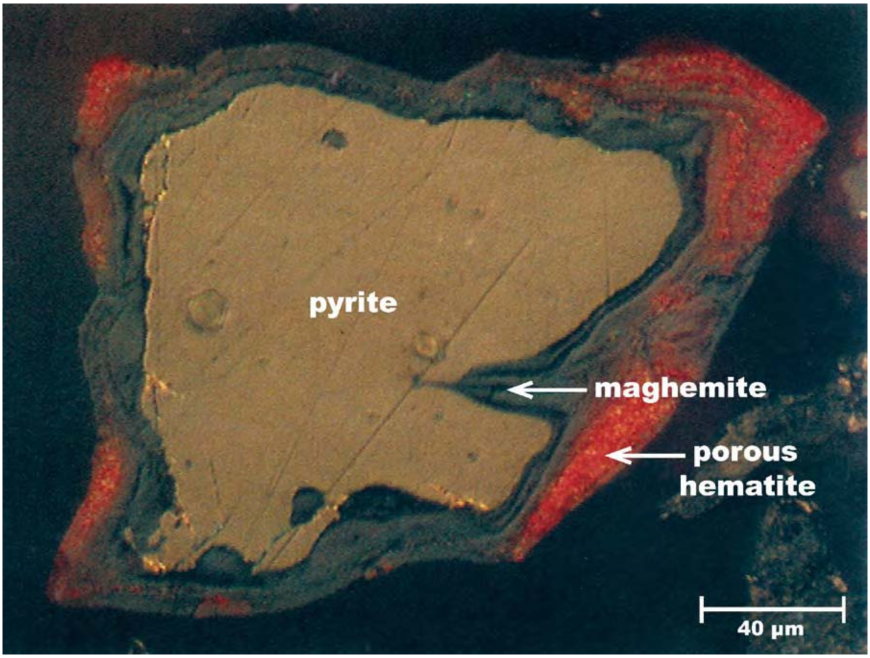

Plate 7. Reaction rims showing the progression in the oxidation of pyrite in the roaster. The core is pyrite [FeS_2], the inner rim is maghemite [Fe_2O_3 with up to 8% Fe] and the outer rim is porous hematite [Fe_2O_3] (Goldstrike, NV, USA).

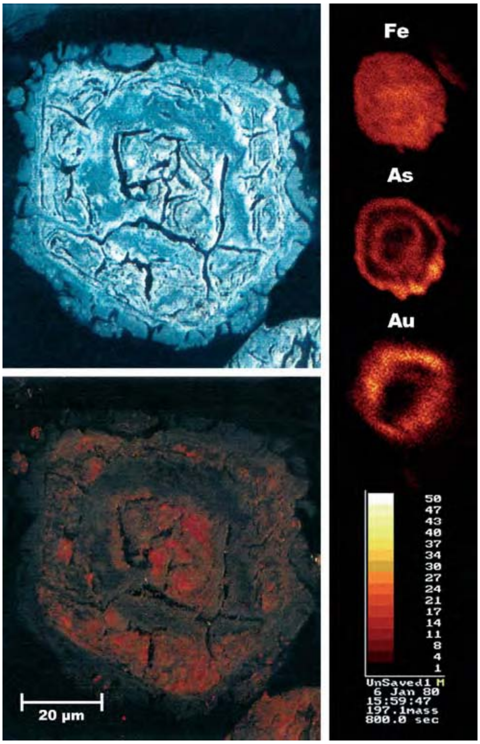

Plate 8. Zoned roaster calcine particle, showing two well-defined maghemite [Fe_2O_3 with up to 8% Fe] zones interbedded with zones enriched in hematite [Fe_2O_3]. Arsenic is strongly enriched in the maghemite zones, and gold is confined the inner maghemite zone. Arsenic is in the form of ferrous pyroarsenite [$FeAs_2O_5$]. Inset: SIMS elemental maps for Fe, As and Au with concentration scale (Goldstrike, NV, USA).

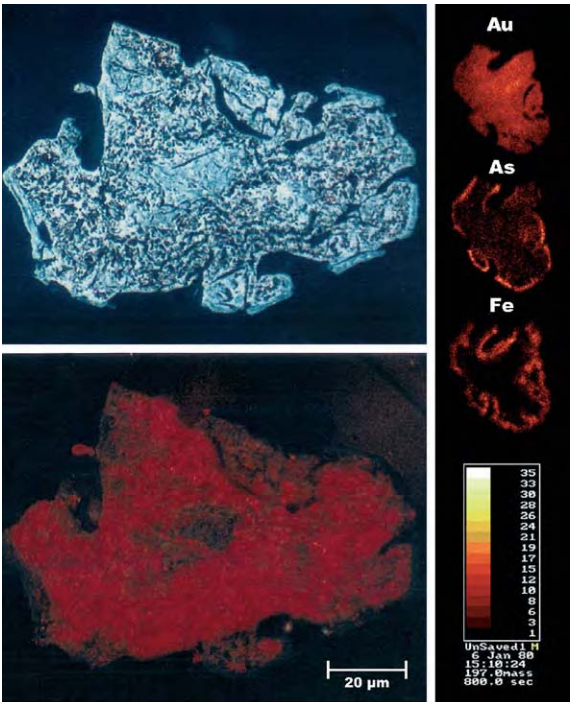

Plate 9. Porous calcine particle with discontinuous sintered rim made of maghemite-ferrous pyroarsenite [$FeAs_2O_5$]. The sintered rim could be a relic of an original Au-rich arsenian pyrite layer coating an As/Au-poor pyrite or the reaction product of As_2O_3 with hematite [Fe_2O_3]. It should be noted that the areas with high arsenic content (yellow in SIMS maps) along the sintered rim are those where maghemite is more obvious in the microscope photograph on the top. Gold is localized along the sintered rim (Goldstrike, NV, USA).

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Chapter 3

Process flowsheet selection

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1. INTRODUCTION

The treatment of gold ores, in particular the competing technologies and their relative advantages and economics, has become a major focus within the industry. A common issue is the increasingly refractory and complex nature of the ores being treated. This chapter gives an overview of the key process options. While it does not purport to be complete, it will hopefully provide a starting point for the process engineer engaged in establishing the optimum flowsheet.

A variety of classifications and definitions of gold ores has been published. Because of the many factors that can impact on the recovery of gold, it is difficult to develop a universal characterization applicable to all gold-bearing rocks. However, La Brooy *et al.* (1994) have provided a useful framework for characterization as shown in Fig. 1.

In this categorization, free-milling ore is defined as yielding over 90% recovery under conventional cyanidation conditions, while those ores that give acceptable economic gold recovery only with the use of significantly higher chemical additions (*e.g.* cyanide, oxygen, carbon) are defined as complex. Refractory ores are thus defined, by exception, as those that still give inadequate recovery. It is implicit in this definition that additional recovery requires some degree of pre-treatment prior to cyanidation. Any further characterization of refractory ores, such as a definition of percentage recovery, is somewhat arbitrary and ignores the impact of economics unique to each specific ore deposit. In terms of this discussion of alternative process routes, the above characterization is adopted.

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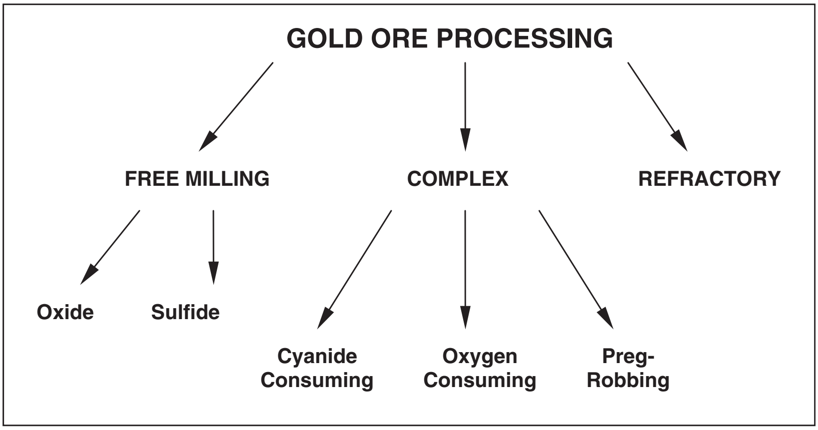

Fig. 1. Gold ore characterization.

Flowsheet selection for free-milling ores can be relatively straightforward, with the key issues revolving around comminution circuit selection, the use of heap leaching, treatment of high-silver ores and flotation options for free-milling sulfides.

Complex ores include those associated with base-metal mineralization, particularly copper, that can consume cyanide and create issues in CIP and elution. The presence of preg-robbing carbon will demand flowsheet inclusions to achieve acceptable recovery without gross losses of gold to CIL tailings.

While refractory characteristics can be seen in a variety of ore types, including auriferous base metals and rocks with a high carbon content, the major focus in refractory gold processing has been on gold-bearing iron sulfides, such as pyrite, arsenopyrite, pyrrhotite, telluride and the stibnite family. It is the intention of this chapter to concentrate on the pre-treatment processes available for the latter ore types.

In summary, gold flowsheet options will be examined under the headings of:

- Comminution processes;
- Free-milling ore processes;
- Complex ore processes;
- Refractory ore processes.

2. COMMINUTION PROCESS OPTIONS

2.1. Overview

Selection of the optimum comminution circuit is arguably one of the most important tasks facing the process engineer (see also Chapter 12). Fig. 2

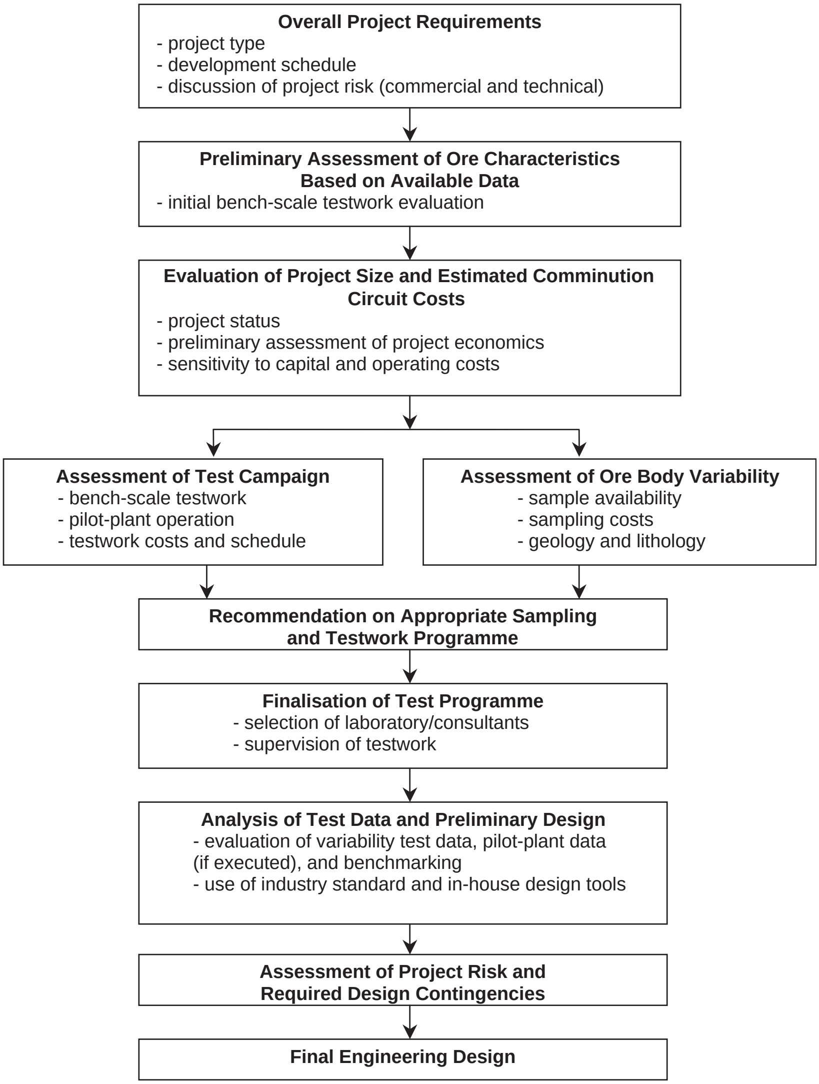

Fig. 2. Comminution circuit decision-making diagram.

illustrates an overall decision-making diagram established by Lane and Lunt (1997) in which the extent of testwork is dependent upon the scale of the project, hence capital cost, and the targeted schedule. For smaller-scale projects with throughputs of less than about 4–5 Mt/a, the costs of piloting can be offset against the provision of flowsheet safeguards and some additional capacity margin. Certain comminution options such as fully autogenous milling and high-pressure grinding rolls (HPGR) usually require piloting regardless of throughput.

Table 1
Matrix of competency and capacity

Competency	Griding Circuit Throughput			
	<0.5 Mt/a	0.5–2 Mt/a	2–6 Mt/a	>6 Mt/a
Low	Single stage SAG	Single stage SAG	Single stage SAG	SAB
Moderate	Single stage SAG or AG	Single stage AG, SAB and ABC	Single stage AG, SAB and ABC	ABC
High	Two stage crush/ball mill	Stage crush/ball mill and SABC	SABC	SABC and stage crush/HPGR/ ball mill

Fleay *et al.* (2002) have provided some excellent guidelines for assessing comminution flowsheet options as illustrated in Table 1 and these and other selection considerations are discussed in turn.

2.2. Ore characteristics

Ore competency and hardness is the prime determinant of the circuit configuration. Low competency may permit the use of lower capital cost crushing and milling equipment such as MMD sizers, single-stage primary mills and SAG mills. High competency will dictate the examination of SABC circuits and, for ores that exhibit extreme resistance to breakage, staged crushing (two or three stages) followed by either ball or SAG milling may have to be considered. At higher throughputs, such circuits can consider the use of HPGRs in place of SAG milling.

Circuits handling moderately competent ores can take advantage of operating cost savings by employing fully autogenous grinding (AG) mills.

2.3. Throughput

As a general guideline, low-capacity projects are driven by the need to minimize capital costs and hence circuit simplicity and minimization of the number of unit operations is a prime goal. Flowsheet considerations include the use of single-stage milling and for soft ores such installations often run in a regime that is intermediate between SAG and ball milling. A further consideration is the elimination of intermediate stockpiling between the primary crusher and the mill. While this may indicate an operating cost increase, it has the potential to again reduce capital. Table 2 illustrates a survey conducted across a number of smaller-scale gold projects that illustrates the achievement of remarkably high plant availabilities.

Table 2
Availability of direct feed milling plants

Project	Location	Plant Size (Mt/a)	Crusher Type	ROM Grizzly Aperture (mm)	Surveyed Mill Availability
Tuckabianna	WA	0.5	48 × 36 Jaw	1500 × 580	97%
Macraes	NZ	1.5	48 × 42 Jaw	710 × 705	>95%
Sansu oxide	Ghana	2.2	750 MMD	700 × 500	>96%
Fortnum (ex Mt. Wilkinson)	WA	0.5	48 × 42 Jaw	1250 × 650	92–96%
Iduapriem	Ghana	1.5	48 × 42 Jaw	700 × 600	93%
Mt. Wilkinson	WA	0.5	None	525 × 535	>90%
Rawas	Indonesia	0.6	42 × 36 Jaw	500 × 875	>90%

With the increase in size of projects and the seemingly inexorable increase in the ultimate capacity of crushers and mills and their associated components, it is worth determining the capacity of a large single-train crusher-SAG mill installation to determine whether this fits with the resource exploitation capability.

2.4. Downstream process requirements

Downstream processes may be sensitive to ore characteristics that are influenced by the comminution circuit such as size distribution and surface chemistry. This is particularly true of sulfide flotation associated with many gold projects where recovery of sulfide, hence precious metal, can be influenced by both parameters. The relative advantages of SAG and AG milling may need to be assessed in such situations.

2.5. Operating cost

Higher capacity projects are particularly sensitive to power, maintenance and steel costs. The designer will need to examine the cost offsets of AG in terms of steel savings against the lower inherent power efficiency.

3. FREE-MILLING ORE PROCESS OPTIONS

3.1. Overview

The recovery circuits of choice are either carbon-in-leach (CIL) or heap leach followed by carbon-in-solution (CIS) (see also Chapter 23). For free-milling ores exhibiting a high gold recovery at a reasonably coarse grind size and with average oxygen and cyanide consumptions, the engineer is faced with few selection issues in determining the flowsheet.

3.2. Site-specific issues

Water quality is an issue to be addressed, particularly in the context of Australian projects. High total dissolved solid (TDS) values influence the performance of the Anglo American (AARL) stripping operation in terms of overall efficiency and can dictate the use of water treatment by softening chemical dosing or reverse osmosis. Alternatively a Pressure Zadra system could be adopted.

Rainfall levels in Western Australia and parts of Queensland are low and, in most instances, all of the water reclaimed from the tailings dam can be recirculated back to the treatment plant. The use of a tailings thickener can minimize the cost of tailings pumping systems while maximizing the recovery of cyanide. In high-rainfall areas, water may need to be discharged to the environment and this will involve some form of cyanide destruction system (see Chapters 28 and 29).

3.3. Gravity-recoverable gold

The benefits of gravity recovery can be readily assessed by undertaking leach tests with and without pre-treatment coupled with mineralogical analysis and examination of gold leach tails solids (see Chapter 13). Early equipment included shaking tables, spirals, drums and other devices. The alternatives expanded to more sophisticated and efficient centrifugal separators such as Knelson and Falcon concentrators with the latter perhaps being more applicable to the treatment of finer solids.

In recent times, a further range of gravity equipment has been successfully commercialized including in-line pressure jigs. equipment development has also extended to the use of high-intensity cyanidation devices (Gekko) to solubilize gold from the concentrates.

3.4. Treatment of high-silver ores

A variety of options are available with the ultimate flowsheet selection being dependent on the ratio of silvergold, the total output of precious metal to be recovered and the solid/liquid separation characteristics of the leached pulp. Further information on the treatment of high-silver gold ores can be found in Chapter 34.

In the event that the mass flow of silver is too high to consider a straightforward CIL-elution-electrowinning circuit, then consideration will need to be given to a zinc precipitation circuit either in combination with CIL or, at very high precious metal outputs, to a full Merrill-Crowe circuit. Allen *et al.* (1998) examined the alternatives for processing Rawas ores having a high silvergold ratio. These findings have been employed, together with GRD Minproc in-house data, to develop the guidelines provided in Table 3.

Table 3
Flowsheet options for high-silver ores

SilverGold Ratio	Flowsheet Options
Low	Maintain typical CIL, elution, electrowinning circuit. Require elevated elution temperature, *e.g.*, Bottle Creek, Pajingo
Moderate	Consider CIL with elution followed by zinc precipitation, *e.g.*, Rawas. Has the potential to produce separate gold and silver bullions
High	May have to opt for full Merrill-Crowe if carbon movement rate becomes impractically high for CIL

The hybrid Merrill-Crowe/CIL circuit is an interesting variant that was adopted at Mt. Muro. This included a single stage of thickening after the gold leach with the overflow routed to Merrill-Crowe and the underflow to CIP. The rationale for the use of this circuit was the poor settlement characteristics of the oxide solids that would have led to a requirement for large thickeners or filters for a conventional Merrill-Crowe circuit. There was also a shortage of real estate at this particular site.

4. COMPLEX ORE PROCESS OPTIONS

4.1. Overview

Complex ores are intermediate between free-milling and refractory ores. As such, they give rise to high usages of cyanide and oxygen and/or are preg-robbing. Speciation of cyanide complexes within leach liquors especially for feeds known to contain copper, zinc, thiosulfates and other complexes is recommended. Flowsheet selection issues are discussed under the following headings.

4.2. Treatment of high-copper ores

Adams (1999) has proposed a classification of gold–copper ores according to the relative concentrations of the two metals. Ores with high copper values are invariably exploited via flotation and smelting with gold recovered in a refinery. The following discussion centres on high gold ores or concentrates treated by cyanidation (see Chapters 32 and 33).

Copper minerals exhibit varying solubilities in cyanide solutions as illustrated in Table 4.

Copper complexes that can be present in cyanide liquors include $Cu(CN)_2^-$, $Cu(CN)_3^{2-}$ and $Cu(CN)_4^{3-}$ with the proportions dependent on the pH, copper concentration and free cyanide concentration. The main issue facing the process engineer is the fact that minimization of cyanide consumption is favoured by the formation of species with a low copper:cyanide mole ratio, *e.g.*, $Cu(CN)_2^-$. However, these species will also load readily onto activated carbon and, at high loadings, can interfere with gold adsorption. In situations where the cyanide-soluble copper levels are low it may be economically feasible to simply raise the cyanide concentration in the leach and thereby minimize the loading of copper. Copper rejection can be further increased by utilizing a cold cyanide elution to preferentially strip the species from the carbon.

At high cyanide-soluble copper levels, however, more specific flowsheet measures will be needed. These can generally be divided into processes that seek to suppress cyanide consumption and those that aim to recover cyanide, and possibly copper as well, from the CIL residue.

The former includes pre-treatment by acid leaching of highly soluble copper species such as oxides and reactive sulfides. Another innovative flowsheet that was originally developed for vat leaching of gold–copper ores in Western Australia involves the use of an ammoniacal cyanide leachant. GRD Minproc also introduced this technique to the Akjoujt gold project in Mauretania.

Cyanide recovery processes (see also Chapter 29) are exemplified by the AVR (acidification–volatilization–regeneration) technology that was introduced at the Beaconsfield gold project in Tasmania (Kitney, 1998). A variant of this process has recently been employed at the Telfer project in Western Australia in the form of the SART (sulfidization–acidification–recycling–thickening) process that recovers both copper as sulfide and cyanide for reuse (Barter *et al.*, 2000).

Table 4
Cyanide solubility of copper species

Copper Mineral		Solubility in CN at 23°C (%)
Azurite	$2CuCl_2O_3 \cdot Cu(OH)_2$	94.5
Bornite	Cu_5FeS_4	96.0
Chalcocite	Cu_2S	90.2
Chalcopyrite	$CuFeS_2$	5.6
Chrysocolla	$CuSiO_3 \cdot 2H_2O$	11.8
Covellite	CuS	96
Cuprite	Cu_2O	96.6
Enargite	Cu_3AsS_4	65.8
Malachite	$2CuCO_3(OH)_2$	99.0
Native copper	Cu	90.0
Tetrahedrite	$(Cu,Fe,Ag,Zn)Sb_4S_{13}$	21.9

4.3. Preg-robbing ores

Carbonaceous ores that exhibit a propensity to adsorb soluble gold onto the naturally occurring carbon pose difficulties (see Chapter 38). Prior to the Penjom project, the process options were largely restricted to two options, *i.e.*:

- The addition of blinding agents such as kerosene with the objective of passivating the carbonaceous material sites.
- Use of large quantities of activated carbon in a full CIL circuit, *i.e.*, a brute force approach to persuading soluble gold to adsorb onto the activated carbon added to the system. While relatively effective this method has disadvantages, in that the circuit requires high carbon inventories and a large elution and regeneration treatment capacity.

The Penjom project employs kerosene but combines this with the use of a commercial ion-exchange resin to adsorb the gold. The advantages of the resin over activated carbon are the much higher equilibrium gold loadings that can be achieved coupled with a greater resistance to fouling in the presence of kerosene. The kerosene addition rates at Penjom were reported to be up to 8 l/t of ore and this compares with usages of up to 500 l/t for activated carbon systems. Further discussion on this option may be found in Chapter 25.

4.4. Oxygen-consuming ores

A number of species, sulfides in particular, consume oxygen to a degree in CIP or CIL circuits and some, such as stibnite (see Chapter 40) and pyrrhotite, can evidence high rates under the conditions that prevail. It is important, in terms of achieving completion of the gold dissolution reaction, to maintain a high level of dissolved oxygen in the leach pulp. A technique that was employed in a number of earlier projects was the use of a high-intensity, air-sparged agitation stage ahead of CIL. This aimed to oxidize the surface of the sulfide mineral thus negating the impact of oxygen depletion in the main CIL system.

Oxygen demand or consumption rate is generally measured by a test procedure originally developed by Lightnin. It entails sparging air or oxygen into a mini cyanidation reactor and monitoring the rate of loss. A minimum concentration of 4 ppm O_2 in an air-sparged system is mandatory and ideally the value should be 8–9 ppm O_2, although some schools of thought target the lower range of dissolved oxygen levels in high oxygen-consuming ores such as from UFG mills to minimize cyanide consumption (see Chapter 20). Table 5 provides a decision-making matrix according to the measured values.

Table 5
Process options by oxygen demand

Classification	Oxygen Demand (mg/l/min)	Options
Low	<0.05	Air injection
Medium	0.05–0.4	Consider oxygen injection
High	>0.4	Oxygen injection via external aerators and/or peroxide addition

It should be noted that there might be other imperatives for the use of oxygen, for example, improved gold dissolution rates. Of the strong oxidizing agents, gaseous oxygen is often preferred as it can be generated on-site and is cheaper than the alternatives if efficient gas dispersion is employed. An advantage of peroxides, such as hydrogen or calcium, is that they can enhance downstream detoxification operations such as the removal of arsenic from solution. The Salsigne gold project in France evidenced exceptionally high oxygen demands and utilized a combination of oxygen in the first two gold leach tanks followed by peroxide in the CIL. This project also employed an aeration device external to the leach tanks to intimately contact pulp and oxygen. A number of equipment types are commercially available.

4.5. Issues associated with mercury

The presence of species other than copper and sulfides may necessitate the incorporation of specific measures to mitigate their impact. Mercury, particularly in the form of cinnabar, leaches readily in cyanide and is of course highly toxic. One method of reducing its dissolution is to limit the cyanide addition as was done at Minahasa but this may not be possible in all situations. Several North American gold projects have faced the issue and have generally used sulfidizing agents to precipitate mercury sulfide from the leach liquor. Precipitants include sodium sulfide and sodium hydrosulfide. Since these are reductants and the gold leach requires oxidizing conditions, they tend to be used towards the end of the leach by which time some of the mercury will have adsorbed onto carbon. Carbamates have also been employed particularly on heap leach liquors where removal of mercury at this point minimizes the extraction onto activated carbon.

Mercury has a low vapour pressure and hence volatilizes at various points in the elution, electrowinning and carbon regeneration operations. The design will need to address this issue in the form of extensive hooding and scrubbing facilities.

5. REFRACTORY ORE PROCESS OPTIONS

The development of the gold mining industry in regions such as Australasia initially focussed on free-milling oxide ores, largely due to the development of improved open-pit mining and gold recovery techniques. With the recognition that many of these deposits continue at depth, but also become more refractory, there has been a sustained interest in the development of improved techniques and processes for these more difficult ores. Much of this development has been driven by the need for more environmentally acceptable process routes and, in particular, the need to dispose of by-products such as arsenic and sulfur in a responsible manner.

Table 6 lists some of the available processes that are either in industrial use or in advanced developmental stages (see also Section II.3 of this book).

In some instances, it may even be appropriate to combine more than one of these processes in a synergistic manner, *e.g.*,

- ultrafine grinding prior to pressure oxidation (Activox®);
- hot caustic leaching of roaster calcines;
- chlorination of carbonaceous oxidation products; and
- biological oxidation of pyrrhotite prior to pressure oxidation.

6. REFRACTORY PROCESS SELECTION

In 1987, when GRD Minproc undertook the feasibility study for the Bogosu project in Ghana, the only refractory gold processes considered to

Table 6
Refractory process routes

Type	Industrial Processes	Developmental Processes
Thermal	Whole-ore roasting Concentrate roasting Smelting	Pyrolysis Flash roasting
Oxidative	Acid pressure oxidation Alkaline pressure oxidation Biological oxidation Nitric acid oxidation	Bio-heap leaching
Chemical	Hot caustic digestion Chlorine Pressure cyanidation	Ammonia leaching
Physical	Fine grinding	Ultrafine grinding

have achieved a suitable stage of development were pressure oxidation and concentrate roasting. Five years later, when evaluating the Sansu sulfide project for Ashanti Goldfields, it was necessary to undertake an extensive evaluation of a number of alternative processes. These included pressure oxidation, biological oxidation, concentrate roasting and the Freeport whole-ore oxygen roasting process, as well as other options such as nitric acid oxidation and ultrafine grinding. The testwork programmes and engineering studies involved in this evaluation took over 2 years to complete at a cost of over US$2 M (Nicholson *et al.*, 1993). Beyond 2000, the number of options has not increased to any significant extent. The focus in recent years has been more on refining the technologies and on developing designs for increased plant capacities.

While it may not be necessary to undertake a detailed programme exploring every option for all refractory gold projects, it is certainly important not to make an arbitrary selection based on pre-conceived ideas of process attributes or on generic comparisons of process economics. In recent years, GRD Minproc has been involved in the selection of refractory processes for the following major projects and, in each instance, the process selection was based on factors unique to each project (refer Table 7).

This diversity of process alternatives demonstrates the importance of considering each orebody on a project-specific basis.

Foo and Bath (1989) have published decision diagrams for the metallurgical testing of refractory gold ores, which provide useful aids to the design of testwork programmes. However, it is important to marry the metallurgical testing with continued economic analyses of each process. Simply achieving high levels of gold recovery at an acceptable cost does not necessarily mean that the optimum process route has been selected.

It is stressed that the selection of the final process route should not be made too early in the assessment process and, especially, without an appropriate

Table 7
Selection of refractory processes

Project	Process Selected
Bogosu	Concentrate roasting
Sansu, Ashanti Goldfields	Concentrate BIOX®
Three Mile Hill	Concentrate fine milling
Macraes Flat	Concentrate fine milling/Pressure oxidation
Kanowna Belle	Concentrate roasting
Minahasa	Whole-ore roasting
Bakyrchik	Nitric acid oxidation
Golden Spec	Pressure cyanidation

level of detail in the metallurgical testwork. In the Kanowna Belle refractory ore study, for example, the ranking of roasting and biological oxidation was reversed between the pre-feasibility and final feasibility study stages, due largely to an improved level of recovery from roasting and lower recovery from biological oxidation, which were both determined in pilot plant testwork. Furthermore, the level of detail in the final study highlighted a greater difference in costs than had previously been determined. In view of the decision of the project owners to take both processes to pilot-plant testing, this reversal in ranking did not adversely affect the timetable for project development and allowed the optimum process selection to be made.

7. FACTORS FOR CONSIDERATION IN REFRACTORY PROCESS SELECTION

Based on GRD Minproc's experience on numerous projects, the following factors are considered to be of importance in selecting a process for treatment of refractory gold ores. All factors should be taken into account at an early stage and process options should be kept open for as long as possible due to the potential for unforeseen issues to impact on the economics of a particular process.

7.1. Gold mineralogy

It is particularly important that the occurrence of gold in the ore is understood at an early stage in the project evaluation (see also Chapter 2). An example in point is the Kanowna Belle project, where identification of the importance of arsenic volatilization allowed roasting conditions to be optimized for gold recovery. Similarly, at the Youanmi mine, identification by various biological oxidation researchers of the occurrence of gold with arsenopyrite, and not with the other, less reactive sulfide minerals such as pyrite, allowed the design of a process in which only a relatively low degree of sulfide oxidation was required to achieve maximum gold recovery.

Association of gold with graphitic carbon can indicate the need for a process such as roasting which eliminates the carbon prior to cyanidation. A recent innovation in this area has been Newmont's high-temperature pressure oxidation process. This has been installed at Twin Creeks in Nevada and has been employed at Macraes in New Zealand (Giraudo *et al.*, 2000) to process finely ground auriferous concentrates. In this process the temperature, oxidation potential and acidity are closely controlled in the autoclave to establish conditions under which the sulfides are oxidized and the carbonaceous material passivated. This project is further discussed in Chapter 37.

A variety of techniques, including conventional mineralogy (Henley, 1991), microbeam techniques (Chryssoulis *et al.*, 1994), electron microscopy and diagnostic leaching, are available and should be used in an integrated approach, both before and during the testwork programme. Such techniques are particularly useful for assessing variations in gold mineralogy throughout an orebody. In the case of an orebody such as Macraes the understanding of the mineralogy has been enhanced through the development of improved methods, such as transmission electron microscopy. It was not until 1997 (Taylor, 1997) that evidence of very fine-grained (sub-micron) carbonaceous platelets was found. Carbonaceous material had long been suspected of contributing to the preg-robbing nature of the ore.

Diagnostic leaching should be used with care and caution, ensuring that the various leach stages are carried out correctly and the results analysed properly. By their nature, refractory ores are difficult to characterize by a limited number of diagnostic leach tests. Applying standard tests to refractory ores can also produce misleading results. Macraes have developed a specific diagnostic leach (Beer, 1994) to evaluate the distribution of gold amongst the various fractions in their orebody.

7.2. Arsenic content

The arsenic content of an ore is important for a variety of reasons. A high arsenic content generally means that a careful assessment of disposal methods is required. Its presence, in significant quantities, virtually eliminates concentrate roasting as a viable alternative because of the high costs in fixing arsenic for safe disposal and the shrinking size of the arsenic market. It should, however, be noted that alternative methods (Lunt *et al.*, 1991; Khoe *et al.*, 1994) are in advanced stages of development and offer the potential for relatively low-cost disposal. This would reduce one of the major advantages for hydrometallurgical oxidation routes. Conversely, a low arsenic content can indicate the potential for high gold recovery from roasting.

A high arsenic content and a low iron content in an ore will indicate the potential for arsenic stability problems following neutralization of oxidized slurries. For BIOX® processing, it has been indicated (Broadhurst, 1994) that an Fe/As ratio of >3 is required to achieve acceptable results. Testwork on the Redox® process (Beattie *et al.*, 1989) has indicated that similar results can be achieved at significantly lower ratios, perhaps due to the greater oxidation potential.

The results of the Sansu project evaluations suggest that, while oxygen-assisted whole-ore roasting is suitable for ores with a low arsenic content, there may be an upper limit beyond which arsenic is not rendered stable within the bed.

7.3. Sulfide content

The sulfide content of an ore can be important for a number of reasons.

Having a high sulfide content proportionately increases the cost of neutralization. A high sulfur content can render discharge to the atmosphere from roasting unacceptable and also adversely impact the economics of an acid plant for capture due to a small local market. Conversely, a high sulfide content can render whole-ore roasting more attractive due to a lower fuel requirement. Use of oxygen significantly reduces the sulfide content required for autothermal roasting. The ratio of sulfide sulfur to the carbonate content of an ore will dictate the need or otherwise for downstream capture or scrubbing of sulfur dioxide from whole-ore roasting, and this is discussed in more detail in Chapters 17 and 18. The viability of pressure oxidation technology is crucially affected by the sulfur:gold ratio. The Macraes pressure leach, for example, is economically viable, despite low gold grades, because the sulfur:gold ratio is also low.

The power costs for oxidation processes, in particular biological and pressure oxidation, are proportional to the amount of sulfur that needs to be oxidized. This will tend to improve the relative economics of processes that are power efficient, such as Redox®, pressure oxidation and, especially, roasting. It can easily be forgotten by the geologists in charge of exploration that the oxidation process will need to be sized not only on the ore throughput, but also on the tonnage of sulfide sulfur to be oxidized. Inadequate information on the variation in sulfur assays throughout an orebody can cause the mine to bottleneck on the oxidation circuit or for capital to be wasted on surplus oxidation capacity.

7.4. Gangue mineralogy

The acid-consuming carbonate content of an ore is of particular significance in process selection. It can impact in a number of ways, including:

- adsorption of sulfur dioxide from roaster operations;
- requirement for acidulation prior to pressure oxidation or during biological oxidation;
- requirement for additional carbonate additions for carbon dioxide levels in biological oxidation if too low; and
- reduction of downstream neutralization costs for hydrometallurgical routes.

The presence of graphitic carbon can be deleterious to a gold recovery operation, due to its preg-robbing potential and its common association with, and occlusion of, gold. Unfortunately, it tends to be preferentially recovered to a flotation concentrate and, hence, concentrate treatment routes are more sensitive to its presence. Roasting processes have the advantage that conditions can be tailored to burn off the carbon prior to cyanidation, as well as using carbon as a part of the calorific balance. However, the higher temperatures required can adversely affect gold recovery due to encapsulation and, if the burning is not successful, the high temperatures can increase the potential for preg-robbing. Other process routes can require its separation by physical techniques prior to oxidation, as is practised at Bakyrchik, or the use of an additional carbon passivation technique, such as the use of CIL to treat carbonaceous BIOX® product, at Sansu.

7.5. Ore variability

Ore variability can impact on process selection in a number of ways. Of particular note is the presence or otherwise of a significant transition or partially oxidized zone. From a metallurgical perspective, this ore type can be the worst material encountered in an orebody, being refractory in nature and also too highly oxidized to allow for good concentration ratios in flotation. Open-pit developments are particularly sensitive to these zones, as they are the first refractory ore to be treated, thus necessitating commissioning to be carried out on, potentially, the worst material. If autothermal roasting is required, the presence of such a zone can be of critical importance to commissioning, as an inadequate sulfur content in the concentrate can prevent roasting operations from proceeding in a satisfactory or economic fashion. Similarly, poor concentration ratios can potentially cause washouts in biological oxidation plants. Treatment of such ore types in Ghana have also encountered high clay contents which have been deleterious to flotation, thickening and filtration.

Flotation of transitional ore types can be improved by such techniques as controlled potential sulfidization, controlled pH flotation, desliming of flotation feed and by increasing the flotation residence time.

As the design of an oxidation circuit is based on the quantity of sulfur to be oxidized, it follows that variations in the sulfide mineralogy will impact directly on plant capacity and operation. Variations in the relative proportions of the various sulfide minerals will need to be taken into account, in particular the presence of the reactive but acid-consuming mineral pyrrhotite ($Fe_{(1-x)}S$).

Planning for the presence of pockets of minerals deleterious to a process is also important. These could include minerals containing metals that are toxic to bacteria (*e.g.*, mercury, lead, *etc.*) or glass-forming minerals in a roasting process.

Another variation could relate to the degree of oxidation required for maximum gold recovery. Some samples can exhibit high gold recoveries at low oxidation levels, while others indicate that maximum oxidation is required.

7.6. Project scale

For most of the oxidation processes, there are limitations on the capacity of particular unit operations. In roasting, the diameter of a roaster is constrained by structural design, while, for biological oxidation, the reactor capacity is currently limited by a maximum agitator size of around 500 kW. Conversely, the relative economics of pressure oxidation appear to increase with throughput, primarily because of fixed costs associated with the ancillary oxygen plant, despite the need for multiple autoclaves. Certainly, the capital costs of processes such as biological oxidation will increase at a higher rate once the maximum reactor size has been reached. The original Sansu BIOX® plant required 18 reactors arranged in three trains and this has subsequently been expanded by the addition of a fourth train and more reactors. Therefore, not only are there fewer economies of scale as the throughput increases; in practice, however, the unit costs increase due to the need for a more complex distribution system of services such as air and cooling water.

High treatment throughputs can also impact in the following ways:

- High consumption of reagents or utilities that can exceed the capacity of the associated infrastructure to support the project. For example, the need to significantly increase the Goldfields Water Supply Scheme to Kalgoorlie to provide high-quality water to a pressure or biological oxidation plant, or the requirement at AGC for large quantities of lime to be imported from Europe due to the limited resources in Ghana.
- Environmental constraints are frequently determined by the quantities of a particular species to be emitted. For example, the licence for the roasters at Gidji, treating concentrates from Kalgoorlie, stipulate the maximum quantity of sulfur dioxide that can be emitted. Similarly, it is probable that if the sulfur output of Kanowna Belle had been much larger, then the permitting of a roaster operation would have been a more significant issue.

7.7. Incremental gold recovery

Several gold projects with which GRD Minproc has been associated display relatively high gold recoveries, say 70–80%, using conventional cyanidation, perhaps with a fine regrind of flotation concentrates. One example is the Macraes Flat mine in New Zealand. In this situation, the incremental process economics are particularly sensitive, especially if the ore grade is low. This tends to favour processes with lower operating costs, such as fine grinding, unless a more expensive oxidation process can provide recovery advantages. The Macraes Flat operation has been a highly successful operation using conventional fine grinding, despite achieving only 70–75% recovery. Ongoing testwork into a variety of processes has shown that higher recovery can be achieved, but until the investigation of Newmont's pressure oxidation process, these did not prove to be economic.

It is GRD Minproc's opinion that advances in fine grinding developed in the base metals industry have the potential to significantly improve the economics of this process through a significant reduction in power consumption.

7.8. Flotation performance

Flotation performance is of great significance in evaluating overall process economics. Indeed, this should be considered as an integral component of the refractory process evaluation. A particular example is the AGC Sansu project, where whole-ore roasting appeared to be relatively attractive until reagent optimization testwork confirmed that higher levels of flotation recovery could be achieved. Other operations have been unable to achieve acceptable recoveries and concentration ratios, and have selected whole-ore treatment routes such as roasting or pressure oxidation, Minahasa being one such example where whole-ore roasting is employed.

The achievement of a satisfactory concentrate grade is of particular importance to concentrate roasting economics. Each ore type needs to be assessed according to its mineralogy to determine which concentration ratios of sulfide and carbon (if present) permit autothermal roasting, *i.e.*, the grade at which no fuel needs to be added for combustion.

The variability in ore types discussed above is particularly pertinent to flotation performance. Indeed, the presence of a significant transition zone can dictate the design of a flotation circuit and the concentration ratio that is achievable, which, in turn, controls the design of the refractory process stage. Achieving autothermal concentrate grades can be particularly difficult in this event.

7.9. Site-specific environmental considerations

The situation in Western Australia, where the discharge of sulfur dioxide was permitted until recently, is unusual and clearly favoured roasting. However, another environmental situation that favoured roasting over biological oxidation at Kanowna Belle was the difficulty in discharging hypersaline water back into the environment, even after cyanide destruction. Due to the sensitivity of the oxidizing bacteria to thiocyanate, it was highly likely that a significant amount of tailings dam decant water would have needed to be discharged, although this would have been difficult owing to its high saline content.

With high arsenic ores, the need for decant water to be discharged rather than recycled is of particular environmental sensitivity. Processes such as BIOX®, which require large amounts of wash water, are particularly affected by this potential issue. In this situation, it is important to test the long-term stability of oxidized products for all base metals and other toxic components. Whilst many can comply with the United States Environmental Protection Agency (US EPA) Toxicity Characteristics Leaching Procedure (TCLP) test, this is not necessarily an indication of long-term stability in tailings dams and other tests should be included in the evaluation procedure.

7.10. Project location and infrastructure

Kanowna Belle and Sansu are important examples of how the project location can have a significant bearing on the selection of a refractory process. At Kanowna Belle, the location resulted in high costs for quality water, power and lime, all of which adversely affected the relative economics of biological oxidation. At Sansu, the choice of biological oxidation over pressure oxidation was highly affected by the remote location and the perceived difficulties in operability and maintainability of the latter process. This compares with Nevada, for example, where the infrastructure has a greater capability of supporting sophisticated processes such as pressure oxidation.

Biological oxidation is relatively disadvantaged when building a plant at altitude, as the inefficiencies of using air to provide the oxidant in a stirred reactor are exacerbated at lower pressures and in the more rarefied atmosphere.

7.11. Water quality and availability

The problems of water quality on the biological oxidation process have been described above in relation to Kanowna Belle. It is important to note that, while the improvements in the process reduced direct water consumption to $8.4\,m^3/h$, the water consumption in the cooling system was still $18.1\,m^3/h$. A hypersaline water-cooling system was developed and pilot tested, but was still considered to be a major risk, as current industrial cooling processes are only operating at chloride levels 10 times lower.

However, the problems of saline water in biological oxidation processes were relatively minor compared with those for pressure oxidation, which required a chloride level of $<150\,mg/l$, lower than that present in the Goldfields Scheme water. The presence of chlorides is believed to result in formation of gold chloride complexes, which then might be reduced to metallic gold.

The potential ability to operate in poor quality water are perceived advantages of processes such as Activox® and Redox®.

7.12. Power costs

In the evaluations described above, the high cost of power in locations such as Kalgoorlie can disadvantage biological oxidation, which has a relatively high power consumption when applied to concentrates. However, at Sansu, the availability of cheap hydro-electrical power meant that this cost differential is significantly reduced and favours large-scale biological oxidation. The ranking of processes according to power consumption changes quite significantly between whole ore and concentrate cases and for different mineralogical compositions.

7.13. Availability of neutralization reagents

The biological oxidation studies for Kanowna Belle were undertaken after the implementation of Gencor's BIOX® process at Wiluna. Both projects are located in Western Australia. However, a significant difference between the two projects is the availability of good quality carbonates close to the Wiluna mine for use in the neutralization step. The nearest occurrence of similar material to Kalgoorlie is over 500 km away, necessitating the use of limestone from Loongana in the Nullarbor region, thereby increasing the operating costs significantly.

The high cost of neutralization reagents can significantly improve the economics of processes, such as whole-ore roasting, which can utilize any carbonate component of the ore for neutralization of the sulfur released during oxidation, or which do not oxidize the ore, such as fine grinding.

7.14. Cyanide consumption and costs

Several process comparisons have focussed on the relative economics of the pre-treatment steps and have assumed that the cyanide consumption in CIL is the same for each process. However, examination of laboratory data in a number of applications has indicated a significant differential in the cyanide consumption, particularly between pressure oxidation and biological oxidation. In some instances, this differential can be as high as 15 kg/t NaCN, which can significantly impact on the process economics due to the increased cost of cyanide destruction in water discharged to the environment.

7.15. Project life

Many of the gold projects in Australia have been initiated on the basis of a relatively short project life, although some of these have outlasted initial predictions. While this situation is less likely to repeat itself as the deposits are extended into the sulfide zones, some of the sulfide deposits are relatively small.

The pressure oxidation process is most sensitive to project life due to the costs of installing the associated oxygen plant. However, the potential incremental recovery and lower operating costs that may be achieved using this technology can counteract the higher capital costs over an extended project life.

7.16. Ability to pilot

It is generally acknowledged that pilot-plant testwork is required prior to installation of a refractory process. This certainly applies to greenfield projects and those where the incremental recovery is high.

Most processes require 200–300 kg of concentrate sample from each major ore type and the testwork programmes can be completed within 1–2 months. Whole-ore processes typically require 500–1,000 kg of sample. In contrast, the biological oxidation pilot programmes can take 4–6 months per ore type and require over 600 kg of concentrate. The reasons for the extended period are the long retention time within the process, which extends the time to examine a particular parameter, and the period required to raise the bacterial activity to an appropriate level.

For some projects, the sample requirements can present problems, especially in situations where the concentration ratio in flotation is high, where there are a variety of ore types to be evaluated or where the sulfide zone is not easily accessed by adits or drilling. As an example, the Kanowna Belle pilot-plant programmes required over 40 t of ore to be obtained from a depth of over 120 m using drilling techniques. A mitigating factor was the relative consistency of the orebody, which permitted the acquisition of a single bulk composite.

In this context, it is also important to ensure that the concentrate sample has a representative grade. While lower grade samples allow some of the sample size requirements to be circumvented, they can produce misleading results. Reagent consumption can be significantly changed, especially if the additional bulk is made up of reactive carbonates. Also, the critical threshold for effects such as bacterial toxicity or vitrification and encapsulation in roasting may not be achieved in a lower-grade sample.

8. DISCUSSION

Evaluation of a number of refractory gold projects has highlighted the need to examine each orebody individually, in terms of both mineralogy and external factors, such as location, size, *etc*. There is not yet any process that has been developed which is as widely applicable to refractory ore treatment as CIP or CIL techniques are to oxide orebodies.

It is extremely difficult to propose a generic programme for the evaluation and selection of a refractory process. These can vary from situations such as that of Ashanti on the Sansu project, where both whole-ore and concentrate processes were highly applicable, necessitating a long and exhaustive evaluation of the alternatives, to one such as Minahasa, where the preliminary testwork programmes and mineralogy demonstrated that whole-ore roasting was a more obvious selection without the need for more extensive studies and testwork.

Perhaps the most important step in selecting a refractory process for a particular orebody is to ensure that the mineralogy and metallurgy are well understood prior to making any decisions. These then need to be considered in the context of the constraints of the process location. It should then be practicable to select a shortlist of suitable technologies for more detailed evaluation.

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Dave Lunt is recognized by the minerals processing industry worldwide as one of the industry's most experienced technical professionals. His career consists of 36 years of operational and consulting experience. David has worked on a wide range of major studies and projects in almost all commodities, including the management and execution of detailed designs and studies for gold (oxide and refractory), copper (oxide and sulfide), uranium, diamonds, nickel laterites and sulfides, vanadium, and other minerals and metals. In addition to his technical experience, David has significant senior management experience having held a number of senior positions with GRD Minproc, including General Manager of the Company's Sydney and Teheran offices. David assumed his current position of Chief Technical Officer in 2002, and also sits on the GRD Minproc Board.

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Chapter 4

Metallurgical testwork: Gold processing options, physical ore properties and cyanide management

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1. BACKGROUND

For the past 100 years the key element in the processing of gold ore has been the cyanidation process. Over the years steady improvements have occurred in equipment design; milling has evolved from stamp mills, through tube mills and ball mills to the large semi-autogenous grinding (SAG) and fullyautogenous grinding (FAG) circuits in modern gold plants. Application of gravity concentration has also waxed and waned over the years but with the development of modern centrifugal machines, this technique has become more popular, and sees a greater variety of equipment alternatives being available than ever before. The advent of carbon-in-pulp in the early 1980s was probably the single most important technological development over the past hundred years. The recovery of gold from refractory ores has also steadily increased over the past 20 years, largely a result of circumstance and necessity, as the easier free-milling gold ores have been depleted. In turn, hydrometallurgical processes, like pressure-oxidative and bacterial leaching, have in many cases superseded traditional roasting practice. The use of resins and alternative lixiviants has also been and continues to be investigated, but as yet these options have not diminished the use of the core carbon-in-pulp (CIP) technology (Fleming, 1981).

Processing of gold ores has become a site-specific choice of techniques and processes, depending upon mineralogical, chemical and metallurgical factors.

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Knowledge of these is important in the formulation of testwork for any gold operation.

All of the above has seen significant changes in the testwork methodology and philosophies that are now in general practice throughout the major gold mining countries. As engineering companies became familiar with gold ore processing and computer modelling became more sophisticated, the need for extensive pilot testing of the CIP process, for example, has largely disappeared. The use of refractory ore treatment options, however, such as bacterial leaching or pressure oxidation, would normally mean that pilot testing of these options is still required, largely because the old adage "no two ore bodies are the same" has never been truer than of these more complex refractory ore types. Other aspects of gold mining have also become more important during early testing and evaluation of gold projects, as general community expectations and awareness have increased. This includes more pro-active cyanide management plans, which inevitably involves a comprehensive understanding of the deportment of cyanide throughout the plant. These will be covered below as we progress through the typical testing options and considerations for a gold project.

Due to the extensive range of test procedures and options available, justice would not be done by describing in detail a select few and there is too much weight of material to describe all. Table 1 gives an indication of the range of typical tests and procedures likely to be considered for a gold programme, and the table has been restricted to tests common or specific for gold.

2. ORE PREPARATION AND ASSESSMENT

Before looking at the fundamentals of gold leaching, the mineralogy and physical characteristics of the subject ore should be examined, as they play an important role in the process options and engineering considerations of the flowsheet design.

2.1. Mineralogical analysis

Mineralogy is an aspect often overlooked, but can be very important if dealing with a metallurgically difficult ore or a known refractory ore. By understanding the mineralogical makeup of the gold bearing and associated species, better-informed decisions can be made with respect to treatment options.

Mineralogical analysis is typically carried out using scanning-electron microscopy (SEM) and X-ray diffractometry (XRD), combined with optical examination by experienced mineralogists (see Chapter 2). The important outcomes of these studies is not how much gold is present, and this can be

Table 1
Typical metallurgical tests for gold ores

Test/Procedure	Batch or Pilot
Activox®	Batch and pilot
Adsorption testing	Batch
Agglomeration and cure	Batch
Amalgamation (typical procedure)	Batch
Amalgamation (for gravity separation concentrates)	Batch
Aqua regia digestion (Bumstead, 1984)	Batch
Bulk cyanide leached and residue gold	Batch
Carbon activity test	Batch
Carbon analysis	Batch
Carbon testing – Wet attrition testing	Batch
CIL bottle roll test	Batch
Column leach for gold (standard)	Batch and pilot
Cyanide – intermittent cyanide bottle roll leach	Batch
Cyanide – large bottle roll cyanidation by crush size	Batch
Cyanide – pressure cyanidation	Batch and pilot
Cyanide – rolling bottle cyanide leach test procedure	Batch
Cyanide – standard cyanide agitated tank CIL leach	Batch and pilot
Diagnostic leaching (Francis *et al*., 1986; Lorenzen, 1992; Lorenzen *et al*., 1986; Lorenzen and Tumilty, 1992; Tumilty and Schmidt, 1986; Tumilty *et al*., 1987)	Batch
Diagnostic leaching flowsheet	Batch
Ferric (standard) agitated vat leach	Batch
Filblast procedures	Batch
Flotation (batch)	Batch
Flotation (continuous)	Pilot
Flotation (locked cycle)	Batch
Gravity concentration – spiral concentrator	Batch and pilot
Gravity separation – Falcon superbowl concentration	Batch
Gravity separation – jigging	Batch and pilot
Gravity separation – Knelson concentrator	Batch
Gravity separation – Wilfley table	Batch and pilot
Leaching – intermittent bottle roll	Batch
Oxygen up-take test	Batch
pH buffer test	Batch
Pressure oxidation	Batch and pilot
Roasting	Batch
Sequential CIP adsorption tests	Batch
Vat leach (standard cyanide)	Batch and pilot

significantly affected by sampling practices, but more the morphology, mineral species association, particle sizes and other metal values present, which may impinge on the overall economics of the orebody.

2.2. Physical analysis

A range of tests is used for assessing the following parameters (Bergstrom, 1985a,b; Bond, 1961, 1963, 1985; Kaya *et al.*, 2003; Millard, 2002):

- Abrasion index (AI)
- Crushing work index (CWI)
- Unconfined compressive strength (UCS)
- Bond rod mill work index (BRMWI)
- Bond ball mill work index (BBMWI)
- JK drop tests
- Advanced media competency tests
- AG/SAG mill index determination.

These tests are crucial in plant design, specification of materials of construction and equipment selection. Engineering companies are generally well versed in these physical test procedures and the generated parameters, which assists with equipment selection and provides the raw data for input into the modelling of process options.

Viscosity testing is also important in terms of material handling (pumping specifications, screening, settling, solid–liquid separation), mass throughput and this extends to tailings disposal or treatment (Dinsdale and Moore, 1962). A range of instrumentation is available with two procedures generally accepted as industry standards. The Bohlin viscometer has wide acceptance for the more typical applications encountered in mineral processing and handling. Vane-type viscometers are becoming more prevalent in determining rheological characteristics of the more difficult ore slurries, or for the more challenging equipment applications, particularly at low stress levels.

Settling testwork goes hand-in-hand with viscosity work and larger column-type work is useful if better simulation of actual working conditions is important, including operating temperatures (Fitch, 1971). Tailings-dam capacity, recycle streams, water balance and mode of waste disposal are all affected to some degree by the solids-settling capacity of the slurries.

2.3. Gravity concentration

Gravity separation, one of the oldest separation techniques, has become increasingly popular in modern plants, with new equipment enhancing the range of separations possible (Laplante and Doucet, 1996). When coupled with generally low capital and operating costs and lack of chemicals to cause environmental concerns, this often provides an attractive process for the recovery of gold (see Chapter 13). Gravity separation relies upon the differences in density of minerals to provide efficient separation. The ease and efficiency of separation is dependent on a number of factors, including relative density, particle size and shape, liberation – all of which affect the selection of equipment type.

In the case of gold, gravity tools can be useful in solving a number of problems. These can include what is termed *spotty* or *coarse* gold, which makes mass balancing and gold accounting extremely difficult. By utilizing gravity ahead of the leach train, early recovery of gold in the process can also have financial benefits and avoid potential losses. Gravity recovery is also a useful diagnostic tool and can, and has been, used to check for the potential *salting* of samples. Removal of coarse gravity-recoverable gold can also enhance leach kinetics in plant practice. Use of gravity recovery as a safety net on tailings has also been exploited at several operations, where unleached gold, either as coarse particles or sulfide locked, are recovered from the tailings by gravity means and re-treated, usually with a re-grind prior to a re-leach.

The range of equipment available for gravity separation includes standard mineral jigs, Kelsey jigs, In-Line Pressure jigs, spirals, tables, Mozeley sizer, Knelson, Falcon Superbowl and others.

2.3.1. *Conventional jigs*

Conventional jigs are often used to recover heavy minerals that are liberated at a coarse particle size from crushing/grinding circuits, thus avoiding subsequent over-grinding and loss.

2.3.2. *Centrifugal jigs*

Centrifugal jigs use enhanced forces generated by their spinning motion to enable finer particle sizes and closer specific gravity (SG) minerals to be separated. The Kelsey jig is the most common example of this type of separator.

2.3.3. *Spirals*

Spirals are one of the oldest gravity separators. There is a wide range of profiles available including low-grade, medium-grade, high-grade and fine mineral models, plus ones incorporating different wash water techniques. Careful monitoring and control of size distribution is important in achieving optimum results with spirals.

2.3.4. *Mozley gravity separator (MGS)*

The MGS is a low-capacity high-performance gravity separator suitable for treating difficult fine particle feeds below 75 μm.

2.3.5. *Falcon and Knelson concentrators*

These are centrifugal type gravity separators also suited to fine particle-size feeds (Ancia *et al.*, 1997). These units come in batch and continuous configuration for both laboratory testing and operational application.

2.3.6. Shaking tables

Tables are often used in the laboratory as a preliminary test to ascertain an ore's amenability to gravity separation or upgrade, or as a tool in their own right. Size of tables used in the laboratory environment vary but usually range from third or quarter production size up to half and on occasion full size.

2.3.7. Super-panners

A laboratory diagnostic tool used to produce the highest concentration of material, super-panners are often used in conjunction with other gravity devices as a final cleaning step, and in the preparation of samples for mineralogical work.

2.4. Cyanide leaching

This is the basis of the vast majority of gold operations around the world (Hedley and Tabachnick, 1968). Almost without exception the following tests are undertaken:

- Standard rolling-bottle leaching is carried out using between 0.25 and 25 kg charges. Larger leaches can also be conducted as required, should better sampling confidence be an issue, or where coarse particles are present.
- Agitated-batch leaching is done using small-scale mixers. Tanks can be covered to minimize loss of cyanide during sparging with air or oxygen. This is an important consideration because these tests are used to calculate reagent consumptions as well as the kinetics of gold extraction as well as final gold extraction. Cyanide, lime or caustic and air or oxygen can constitute some of the largest operating costs in a simple gold operation.
- Monitoring is usually carried out at regular time intervals to control pH, cyanide concentration and dissolved oxygen. Samples of solution, solids and carbon can also be taken to measure leach rates.
- Large-scale batch or continuous cyanide leaching (piloting) can be conducted using a range of hydrometallurgical pilot equipment.

Unless the ore is *preg-robbing*, the batch cyanide leach tests are normally done without the addition of carbon. An exception would be in the case of a continuous run, whereby the absorption part of the process would also be tested, hence the use of counter-current carbon contacting. *Preg-robbing* is a term used to describe an ore slurry containing material that has a capacity to adsorb gold (see Chapter 38). It may be naturally occurring carbon or a clay-based mineral. Thus as the gold is dissolved by the cyanide it is absorbed by the preg-robber, and solution assay monitoring will show a low or barren gold tenor. In these cases activated carbon is added upfront (carbon-in-leach), which should preferentially adsorb the gold as it is dissolved from the ore, and thus enable a determination of gold recovery to be made.

Should alternative lixiviants be a consideration, such as in thiourea and thiosulfate leaching, then similar tests to the above are required, together with some specialized analytical procedures given the different chemistry involved.

Gravity recovery is often examined in conjunction with cyanidation, usually when there is significant coarse-free gold present. Removal of this gold enhances the leach kinetics of the remaining finer gold, enables quicker recovery of gold in practice, avoids gold being held up in plant *gold traps*, and makes for better representative sampling of both leach feed and tailings.

2.5. Heap leaching

The recovery of gold from heaps or dumps is often seen as a specialty area of gold metallurgy, or at the least, gold processing (Van Zyl *et al.*, 1988). A requirement to be able to scale up from laboratory tests to field application has seen the need to develop specific procedures and techniques, in order to facilitate this and minimize risk. Column leaching (to assess heap-leaching potential) is conducted using a range of available columns, from 100 mm diameter × 3 m high to 1,000 mm diameter × 6 m high. Agglomeration of clay-type ores is done using rotating drums. Percolation studies are also undertaken to ensure that an efficient flow of leaching solution can be realized with the particular ore type being examined. Poor percolation can have severe ramifications during the running of heap-leach operations. Recirculating leach streams are also seen as an important feature of these tests, again to mitigate the risks of operating a full-size heap leach.

2.6. Recovery from solution

Most work that is carried out in the recovery of gold from solution involves the use of carbon in CIL or CIP configurations.

- The sequential CIP test is carried out to assess the rates and extent of gold leaching and loading for new ore types, generating Fleming kinetic parameters k and n.
- The full range of ASTM carbon tests should be carried out to keep a check on the quality of new and regenerated carbons, while maximizing gold adsorption and elution efficiencies. Some of the parameters that are measured include:
    - Activity (*e.g.* Fleming constants k and n, Calgon constants M and R)
    - Ball pan hardness
    - Apparent density
    - Moisture determination

  - Elution profile
  - Chemical analysis
  - Attrition rates
  - Ash content.

Procedures for the above tests are covered in the literature references or are common generic laboratory procedures found in most commercial test laboratories. Zinc cementation tests are also conducted for operations using Merrill-Crowe circuits.

Some new types of resins have recently been tested as alternatives to carbon in special applications, including preg-robbing ores and those with high base-metal content.

2.7. Cyanide speciation

The toxicity of cyanide in mine tailings and effluents is very dependent on the speciation of the cyanide present (Adams, 2001). Growing concerns over the use of cyanide has seen the development of analytical and consulting services to assist in the measurement and interpretation of cyanide speciation. Analyses include total cyanide, weak acid dissociable (WAD) cyanide, free cyanide, thiocyanate, cyanate, pH, Eh and total metals, from which the whole range of metal cyanide complex speciation is obtained. This information is essential in the choice of appropriate cyanide removal or recovery technologies.

2.8. Flotation

Certain gold ores, mainly those containing sulfides, arsenides or tellurides, are best treated by producing a flotation concentrate (Anderson, 1980; Jones and Woodcock, 1984; King, 1982). This is almost always the case in treating refractory gold ores, where the refractory nature of the ore is due to sulfide mineral species. It is also the case where it is desirable to reduce the mass of material that needs to be treated to recover the gold, or where differential flotation is used to produce a separate concentrate of a valuable metal (*e.g.* copper), which co-exists with the gold, and which would otherwise hinder the recovery of gold. A separate gold concentrate is then produced for further processing.

While flotation is one of the mining industry's oldest and best-established processes, it is still prudent that a test programme would encompass batch tests through to continuous pilot-plant campaigns. Typically, this would entail conducting a series of batch tests using Denver, Agitair or equivalent bench-scale machines on samples of ore of around 500–1,000 g. These tests are done to examine differing reagent schemes and stages of flotation. Tests on the various ore types likely to be encountered during mining are also done at this scale once the flotation scheme has been determined. Piloting is typically conducted at feed rates of 100–1,000 kg/h, and the equipment used simulates the actual plant flotation flowsheet to ensure that any recirculating streams are acceptable and to give a greater level of comfort to the engineers and mine owners that target production in both grade and tonnage is achievable. Piloting is also conducted to produce sufficient quantities of concentrate for downstream processing studies. These could include bacterial leaching, roasting or pressure oxidation.

2.9. Filtration and settling

Many ores, particularly those with significant clay content, may experience difficulties with filtration and/or settling. A range of batch tests are available to assess these unit operations, while pilot counter-current decantation (CCD) circuits are generally utilized only if the downstream flowsheet requires it. Test programmes are often carried out in conjunction with suppliers of equipment or chemical additives.

2.10. Cyanide detoxification

As with the general concerns on the use of cyanide, testing and consulting services in the area of cyanide detoxification have become more prevalent. The common technologies include SO_2/air, hydrogen peroxide, Caro's acid and ferrous sulfate additions, as well as bacterially assisted detoxification. Cyanide recovery technologies such as acidification–volatilization–regeneration (AVR) and resin and carbon adsorption are also often considered. The most appropriate choice of detoxification technology and/or recovery options is growing in importance and is based around economic and environmental compliance factors.

2.11. Refractory gold ores

A range of treatment possibilities for refractory ores is now available, with many more being developed (Lorenzen and Van Deventer, 1992; Malhotra and Armstrong, 1996). The more accepted processes include:

- *Pressure oxidation:* The conventional process operates at around 180–220°C at pressures in excess of 2,000 kPa. There are several commercial plants in operation using this process. The Platsol® process also operates in this range of temperature and pressure and has been considered for applications when PGMs are present. Testing involves batch tests to firm up optimum parameters, followed by continuous pilot-plant testing. Activox® oxidation is a low-temperature version of pressure oxidation, and is also tested by batch and continuous piloting. The Cominco Engineering Services Ltd. (CESL) process is a proprietary process developed by Cominco that involves pressure leaching with chlorides as the oxidant.

- *Bacterial oxidation:* Significant publicity has been afforded this process option and several commercial plants are in operation. Both batch and pilot-scale vat leach tests are undertaken and a range of bacterial types have been applied. This technology has been extended to heap leach applications as a result of developments in agglomeration techniques. Agglomerated column-leaching tests are utilized to examine recoveries and reagent usage.
- *Roasting:* This is generally tested on a small scale in muffle furnaces or rotary kilns. Unless considering building an acid plant, this process is losing favour for environmental reasons.
- *Ultra-fine milling (UFM):* Some pyritic ores contain fine particulate gold that is liberated by UFM below 20 μm. UFM is carried out using stirred mills, attritors or pin mills, and accurate power requirements and media usage are critical.
- *Copper-rich ores:* Depending on the levels of copper and its mineralogy, the processing of copper-rich ores, can include flotation, selective leaching, CIP, elution and electrowinning (EW)

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Chapter 5

Process simulation and modelling

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1. INTRODUCTION

Simulation technology has been used in the gold industry for over two decades. It is firmly established in the engineering and design field, and is most commonly used to produce steady-state mass and energy balances. However, there are many other reasons to consider simulation in the industry, such as:

- To design and then test process control strategies;
- To train plant operators on both new and as yet unbuilt processing plants as well as on existing operations;
- To predict the effect of changes on existing plants;
- To debottleneck existing plants, and
- To characterize the physical behaviour of the process solids or fluids.

Process simulation involves building a model either of a single area of the gold recovery plant or of the whole operation, usually using specialized software tools. This model will respond to given inputs much as the operation would be expected to behave in the real world. Using it the engineer can experiment, testing various ideas and options to get an understanding of how the actual operation would behave in certain situations. It can be used to size new plant and equipment, trial new equipment or control strategies and to see how the system will perform at different loads or ore blends.

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By simulating the process plant closely the process engineer can remove a large amount of uncertainty from engineering decisions. Modelling for decision support is therefore becoming a project requirement in the gold industry.

As an example of the use of simulation, consider a design team that is contemplating optimizing the milling and classification plant of a gold recovery operation, but it is not known if the potential gain in productivity would justify the engineering cost. It certainly would not be cost-effective to make the changes and then remove them later if it does not work out. However, a careful simulation study could shed some light on the question by simulating the operation of the plant in its current configuration and as it would operate with the proposed changes.

However, before diving into a simulation, the engineer must first determine the key objective of the simulation and second have a very good idea of the amount and reliability of data available for the simulation. These two points are of utmost importance to any modelling project, but are often overlooked. Many modelling projects have gone off the rails before the first unit is inserted on the computer, owing to a lack of planning.

2. BENEFITS OF SIMULATION

Simulation has a continual application for decision support in all facets of a project, from the conceptual design, through the development, implementation, commissioning and operational stages.

Simulation is being recognized more and more by top-level management as tool to assist with risk reduction and protection of investments. The investment may be an existing gold operation, or a new resource. Simulation, in this context, is used as a decision-support tool to verify and optimize capital expenditures to meet the objectives of a new project or system modification. By modelling the system the process engineer reduces the surprises that can happen in designing complex systems.

When presenting the results of simulation to management the use of animation, inherent in most simulation tools, is a strong communication tool. It helps people who are not involved in the technical aspects of a project to gain a better understanding of the proposed process design. In addition, animated simulation models give management, or clients, confidence that the proposed system will perform in the real environment.

Process engineers can use simulation as a cost-savings and cost-avoidance tool during the design phases of a project. It allows the designers to ‘test drive’ and optimize a system before a design is finalized and implemented.

The following design aspects can be verified using various process simulation packages:

- Plant throughput;
- Potential or existing bottlenecks;
- Plant control philosophy;
- Materials handling issues involving continuous processes such as conveyors, or discrete processes such as haulage trucks; and
- Optimization of plant layout.

Simulation models are generally statistically based, so they can more realistically reflect a system operation. Thus, by conducting a number of 'what if' analyses, the decisions based on simulation of an operation are much more accurate than spreadsheet or hand calculations.

The number of clients, or resource developers, that require some form of process simulation before committing funds to a project is increasing. An independently verified simulation model increases investor confidence in the proposed process or optimization.

However, there has been some resistance to even wider acceptance and usefulness of simulation in the gold industry. First, models used to study metallurgical systems tend to be very complex, and writing computer programs to execute them has been an involved and time-consuming task. This task has been made much easier in recent years by the development of excellent software packages that automatically provide many of the features needed to build a simulation model. A second problem with the simulation of complex systems is that a large amount of computing time is sometimes required. However, this difficulty is largely becoming irrelevant as computers become faster and cheaper.

Application areas for process simulation are thus numerous and diverse; however, there are several other problems encountered on gold operations for which other forms of simulation have been found to be useful:

- Determining hardware and software requirements for computer control systems;
- Designing and optimizing transportation systems such as underground haulage trucks, and
- Designing and optimizing underground water and air reticulation systems.

In order to model any unit section, or an entire gold operation, the modeller often has to make a set of assumptions about various aspects of the plant. These assumptions, together with the available data constitute a model that is used to try to gain some understanding of how the operation will behave.

3. ALTERNATIVES TO COMPUTER SIMULATION

There are several alternatives to computer simulation that can be applied:

3.1. Experiment with the real plant operation

If it is possible and cost-effective to alter the plant physically and then let it operate under the new conditions, it is preferable to do so, for in this case there is no question about whether what we study is valid. However, it is rarely feasible to do this, because such an experiment would often be too costly or too disruptive to the plant. For example, an operation may be contemplating reducing the number of ore trucks to decrease costs, but actually trying this could lead to disruption of the hydrometallurgical plant. A further scenario may be that the operation does not yet exist, but we nevertheless want to study various flowsheets to optimize the plant design. For these reasons, it is usually necessary to build a model as a representation of the operation and study it to determine optimal plant configuration. When using a model, there is always the question of whether it accurately reflects the operation for the purposes of the decisions to be made. This is why an independent party should validate all input data and assumptions used to build the model.

3.2. Build a physical model

To many people, the word *model* evokes images of scaled-down versions of buildings, or miniature vehicles. These are examples of physical models, and are not typical of the kinds of models that are usually of interest in operations research and systems analysis. Occasionally, it has been found useful to build physical models to study engineering systems such as a tabletop scale model of a material-handling system. However, the vast majority of models built for such purposes are *simulated,* representing a system in terms of logical and quantitative relationships. These are then manipulated to see how the model reacts (and thus how the plant would react) if the mathematical model is a valid one. In the gold recovery field these simulation models are far more useful than physical models.

4. CLASSIFICATION OF SIMULATION MODELS

Gold operations can be categorized to be one of two types, discrete and continuous:

- A *discrete* operation is one for which the variables change instantaneously at separated points in time. An ore-haulage system using trucks is an example of a discrete operation, since the variables, for example, the number of trucks with ore, change only when a truck delivers or receives a load of ore.

- A *continuous* operation is one for which the variables change continuously with respect to time. A comminution and classifying operation is an example of a continuous operation, since variables such as tank level and slurry density can change continuously over time.

Few operations in practice are entirely discrete or continuous, but since one type of change predominates for most operations, it will usually be possible to classify an operation as being either discrete or continuous.

It is also useful to classify **simulation models** into different types:

- *Steady-state simulation models*. A steady-state simulation model is a representation of an operation that has reached a steady operating point. Time does not play any part in the simulation. The model represents the operation at a fixed point in time, normally when the plant has reached equilibrium.
- *Dynamic continuous simulation models*. A dynamic simulation model represents an operation as it evolves over time, such as at start-up, shutdown and under unsteady conditions.
- *Computation fluid dynamic (CFD)* models are a subset of continuous models. This type of modelling uses advanced computer software to model the flow of fluids in a vessel or, less frequently, through a processing facility. The fluid modelled may be a liquid, gas or loose particle, or any combination of the three.
- *Dynamic discrete simulation models*. Discrete simulation is used to model operations where individual items change location or form with time, such as an ore-haulage system using trucks. It should be noted that a discrete model is not always used to model a discrete operation, and vice versa. The decision whether to use a discrete or a continuous model for a particular operation depends on the specific objectives of the study. For example, a model of the ore truck haulage operation would be discrete if the characteristics and movement of individual trucks was important. Alternatively, if the movement of the trucks could be averaged over time then the flow of ore could be described by differential equations in a continuous model.

5. STEADY-STATE CONTINUOUS SIMULATION

There are a number of software packages that are available to the process engineer and have been customized to handle steady-state simulations. These have a variety of specialist uses and some of these will be discussed later as they fit into an overall gold plant design.

5.1. Comminution and size separation

Successful recovery of gold from the ore is very strongly influenced by the size to which the ore is ground prior to processing (see Chapter 12). All gold ores vary, depending upon their location, weathering and other factors, and as such there is no 'standard' comminution circuit. However, Fig. 1 below shows a fairly generic comminution circuit that may be used to grind gold-bearing ore.

Mills are one of the most expensive items of equipment to install and operate on gold plants and the quality of the grind achieved in the comminution circuit is critical to recovery processes downstream. Therefore, it is vital that this area of the plant is designed and operated efficiently. Process simulation is now used extensively in both the design of new comminution plants and also in the optimization of existing operations.

When optimizing or designing a comminution circuit, the process engineer requires specialized software that can predict changes to ore breakage as the circuit flows and/or equipment configurations are changed. This is only possible if a sufficient quantity of sample is tested and analysed to obtain breakage functions for the specific ore in question. Since no two ores are identical, it is not possible to use the results from similar operations and expect accurate, or even representative results. Therefore, when designing a new milling circuit it is essential that sufficient sample of representative ore is obtained for testing. The information obtained from the testwork is then used in the process simulation. It is useful here to repeat the modeller's golden rule, *Garbage In = Garbage Out*. Nowhere is this adage more true

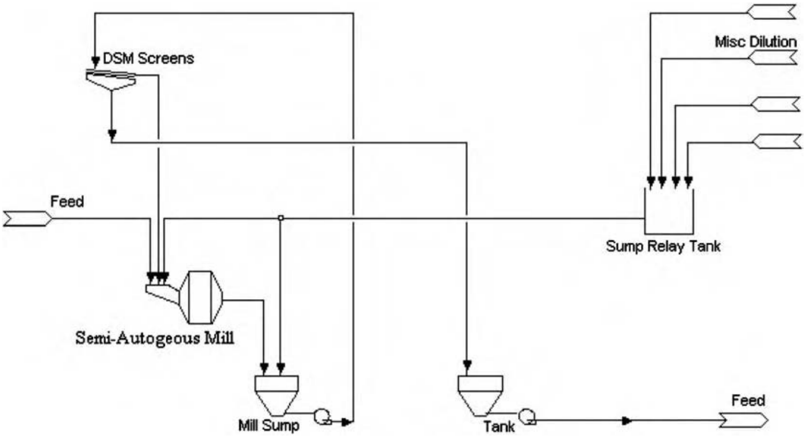

Fig. 1. Example of a comminution circuit flowsheet.

than with simulation of comminution circuits. This means that it is essential that time and effort are expended in obtaining representative samples of ore and using these to obtain the required grinding and breakage characteristics required. Obtaining samples and/or data will be a lot more straightforward when optimizing an existing circuit. Nevertheless, this aspect of the optimization must not be overlooked when embarking on a simulation of an operating plant.

A further item that must be defined before running the simulation is the actual required capacity of the operation. This is usually decided by ore reserve and economic factors and is quoted in tons per annum (*tpa*). However, equipment sizing, and hence simulations, are normally based on tons per hour (*tph*) and hence the conversion between *tpa* and *tph* must be carried out. The plant availability is the factor that is required to carry out this conversion. This is no minor operation, as plant availability has traditionally been a subjective value. It is based on past experience, vendor guarantees, the location of the operation and amount of stand-by equipment installed, amongst other factors. Availability factors quoted for comminution circuits are normally between 93 and 97%. This must be clearly stated within the criteria for the simulation, together with any supporting data.

Once the required information has been obtained, the simulation of the comminution circuit can be run. There are a number of simulation tools available to the process engineer and these include the following options:

- *Vendor packages*. The mill and crusher vendors have computer packages, which they will run to determine optimum equipment size and power requirements. This can be a useful starting point and will typically be used when the engineer discusses equipment and process guarantees with the manufacturer.
- *Speciality comminution software.* These packages have been written specifically to simulate comminution and classifying equipment. The following specialized process models are typically available in the packages:
  - Rod mill;
  - Ball mill;
  - Autogenous mill;
  - Semi-autogenous mill;
  - Cone crusher;
  - High-pressure grinding rolls (HPGR) crusher;
  - Two-rolls crusher;
  - Jaw crusher;
  - Single-deck screen;
  - DSM screen;
  - Hydrocyclones;

  - ○ Rake classifier, and
  - ○ Spiral classifier.

The mill and crusher vendors usually have a large amount of information on breakage functions and the behaviour of classification equipment. For a specified circuit, the simulation software can be used to predict the following information:

- Solids and water flowrate in all streams in the circuit;
- Size distributions for all streams in the circuit;
- Power draw for crushers and grinding mills;
- Operating pressure for hydrocyclones; and
- Charge load in autogenous grinding (AG) and semi-autogenous grinding (SAG) mills.

These packages have been written as a tool for process engineers where modelling is only an occasional part of their job function. Therefore, they are reasonably user friendly with windows-based graphical interfaces and menu-driven options. They must be used with the same amount of caution as any other simulation package, and the results obtained from the modelling must be scrutinized with a critical eye.

One of the most widely used comminution software packages in Australia is *JKSimMet*^{TM}, which is often the software package of choice of process engineers involved in comminution circuits. This package has been used successfully on many gold projects around the world.

5.2. Recovery of gold from ore

Once the gold ore has been milled to the required size, usually on the order of P80 of 70 µm, it is generally thickened and pumped to the leach circuit. The plant may be a carbon-in-pulp (CIP) or carbon-in-leach (CIL) followed by elution and then recovery of the gold via electrowinning or precipitation. No matter which route is chosen for the hydrometallurgical recovery of the gold, the design or optimization of the plant will require some form of a mass balance.

The main process flowsheet for a gold plant is not overly complicated, with very few recycle streams, and hence a mass and energy balance of the process is not too arduous. This can be carried out using hand calculations or a simple spreadsheet and this may be sufficient for a first pass of the design. However, this is not recommended for a truly robust design for a more complex circuit flowsheet.

A simulation model requires that all of the processes in the plant be defined and configured. This approach is very useful; to develop the model the process engineer must include all of the area and unit details. This has significant advantages over hand calculations or spreadsheets because the model does not allow omissions and forces the engineer to state any assumptions used in defining the model.

With the widespread availability of reasonably priced steady-state simulation packages it is becoming accepted practice to use one of these to produce the mass and energy balance. These packages are relatively user friendly and generally have extensive chemical and physical databases, allowing the process engineer to produce a simulation model with the minimum of fuss. Once the model has been constructed and validated it can be used to optimize both the main process flowsheet and the utilities, such as water, reagents, *etc.*

There are many advantages of producing the mass and energy balance of the recovery plant using a steady-state simulation rather than via a spreadsheet:

- The process can be easily audited and validated;
- The underlying algorithms are not open to change, as would be the case in a spreadsheet;
- Changes can be implemented relatively smoothly; and
- The simulation model provides a graphical representation of the process.

In addition to all of these advantages, it is possible to extend the steady-state simulation model to the next stage of simulation – either full or pseudo-dynamic model. The advantages of this will be discussed in the following section. Some of the simulation packages that are used in the gold industry to produce steady-state models are:

- *Metsim* – this package includes a chemical species database and is used throughout the world for mass-balancing purposes. Add-on modules also include a heap-leach capability, for example, which is useful for modelling this area of a gold plant, if required.
- *SysCAD* – this package has the advantage of being both a steady-state and dynamic simulation package. Hence, it can be used to produce a mass and energy balance, which can be extended into the dynamic world, if required.
- *Ideas* – this package is relatively new to the metallurgical industry.

6. DYNAMIC CONTINUOUS SIMULATION

A dynamic simulation model can be a powerful tool for the process engineer, as the model can represent the behaviour of the gold operation over time. The benefits provided vary, depending on the project details and the stage of engineering, from preliminary design to on-line optimization.

There are a number of results that can be achieved with dynamic process simulation that cannot be done with traditional or steady-state simulation:

- Sizing of surge capacities, such as stockpiles or surge tanks;
- Equipment sizing and configuration;
- Determining plant availability, based on maintenance and breakdown information;
- Testing unsteady state conditions, such as start-up and shutdown; and
- Developing and testing control strategies.

The last point above, relating to the control system, is often neglected when defining the application of dynamic modelling. A dynamic model can be used as a tool to help design, test and tune a control system. The control system developed can then be used as a basis for the functional descriptions and detailed specification for the control strategy.

Once a model has been developed, the engineer may then run a number of test scenarios. Each scenario may be configured differently, such as different feed conditions, different unit configurations, different control strategies, etc. The information that can be generated includes:

- Maximum and minimum values and averages for variables such as bin levels or conveyor loading;
- Utilization or efficiencies of specific units;
- Amount of downtime or operating time for specific units (availability); and
- Various control system effects such as alarm occurrences, states or modes of operation.

In the past, dynamic process simulation has required relatively sophisticated software packages and high-speed computers. This, together with the large amount of data required to develop a dynamic simulation, has limited its use in the gold industry. However, with the advances in both computing speed and simulation software it is now possible to produce a *pseudo-dynamic* model of an operation. This allows the process engineer to gain most of the advantages of dynamic simulation using a standard personal computer (PC), without having to specify every last detail of the piping network.

Some of the simulation packages that can be used to produce dynamic models are:

- *SysCAD* – This package has been widely used to provide dynamic simulations for applications such as operator training, control system design testing, air and water reticulation in underground operations and confirming metallurgical plant availability.

- *Ideas* – This package has been used in North America for dynamic simulations.

7. DYNAMIC DISCRETE SIMULATION

As the name implies, discrete simulation involves modelling events that can be viewed as individual events moving in time. This form of simulation is extremely useful for modelling the 'front end' of a gold operation, *i.e.* the movement of ore within the mining operation and from the mine to the metallurgical plant. This may involve road, rail or conveyor transport of the ore and the stockpiles. It may also be used for the 'tail end' of the plant, where the gold is purified and handled as discrete packages.

Discrete simulation modelling has been used to assist in both mine planning and the development of strategies for the internal transfer of ore within mines. This includes both underground and open-pit mines. Modelling provides an understanding of the complex interactions in the materials handling systems and allows operating procedures to be developed to improve productivity.

A well-developed discrete simulation can be used to predict operational performance of a new mine, or improvements to the efficiency of an existing mine resulting from changes to layout or haulage systems. A wide range of parameters can be investigated to determine the optimal system. These include number of trucks, truck capacity, haulage times, number of passing bays, delays in loading and unloading trucks, *etc.*

Some of the simulation packages that can be used to produce discrete dynamic models are:

- *Arena* – This package has been widely used to provide discrete simulations for ore haulage systems on gold operations throughout the world.
- *Planimate* – This package was developed in Australia and has been used extensively in this country.

8. COMPUTATIONAL FLUID DYNAMICS

Dynamic simulation using Computational Fluid Dynamics (CFD) is being employed in a drive to improve gold recovery. The CIP or CIL processes are extremely important in determining the overall recovery of gold from the ore.

Because the gold is adsorbed onto the carbon particles in the leaching tanks, it is very important that the tanks are well mixed, so that the gold and carbon in solution have a good chance of interacting.

CFD modelling is used to determine the distribution of the gold and carbon particles with the leach vessels. The data required for the modelling includes, at the very least, the vessel dimensions, impeller characteristics, and slurry characteristics, such as viscosity and density, as well as the particle size of the ore and the carbon.

The CFD software is used to convert these data into a complex model of an individual vessel, showing the amount of mixing achieved and also any areas of little or no mixing. The results from the simulation work can be represented in tables and graphs and also as a graphical three-dimensional representation of the flow within the vessel.

If there are areas of little or no mixing within a vessel, CFD can be used to predict the flow patterns if changes are made to the impeller, or baffles added or changed in the tank. This allows the engineers to implement the changes with a degree of confidence that mixing will be improved.

9. THE FUTURE OF PROCESS SIMULATION

Advances in process simulation software and computer processing speed over the last few years have meant that the use of simulation in the gold industry has increased dramatically. This has been mainly in the use of steady-state simulation to produce mass and energy balances and discrete simulation for the modelling of mining operations; various modelling packages are also available for the modelling of geology (*e.g.* Datamine (exploration), MRO (mine reserves optimizer), Vulcan (pit design) Whittle (pit optimization). The model is a comprehensive store of knowledge representing the process design, control, stream flows, operation, properties, etc.

Below are some of the innovations that are being implemented, or are in an advanced stage of design in the computer simulation field:

- Intranet simulation solutions that allow users to access a process model from anywhere on an operating plant, or within a company. Here the process simulation is ‘transparent’ and the users do not require any specialist modelling experience. The interface between the user and the simulation may be via a spreadsheet or drop-down menus and user requests are queued as per print requests. This allows such diverse users as financial analysts, operations personnel, area engineers or line managers to manipulate a process model for any number of different scenarios;

- Fully integrated mine-to-product simulations that include both discrete and continuous dynamic simulations, and
- Automatically generated simulation models based on computer databases.

Heather Smith has over 18 years of experience in the metallurgical industry. This experience has been gained mainly in South Africa and Australia, but includes various projects in Europe. She has taken the role of lead process design engineer for a number of process engineering projects. These have included solvent extraction, ion exchange, platinum concentrators and plant automation projects. Heather's main area of interest is in process simulation. She has taken the lead in this area for a variety of projects including nickel and alumina refineries, an offshore refinery training simulation, water reticulation systems and numerous other metallurgical plants.

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Chapter 6

Feasibility study plant design

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1. INTRODUCTION

There are a number of key objectives in completing the process plant design for a feasibility study:

- The design must be feasible and constructible.
- The design must focus on the key issues that drive the capital and operating costs.
- Only sufficient design is completed to provide backup for the capital and operating cost estimates at the appropriate level of accuracy to establish the feasibility of the design.
- The feasibility study design may identify a number of issues needing resolution at the detailed design stage.

Every study is different and has a number of project-specific factors. This chapter provides an overview of some of the key drivers for the process plant design on an area basis. It is not intended to be a manual of plant design.

2. GENERAL SITE ISSUES

A number of general site issues need to be considered in a feasibility plant design.

1. Site location and access. A remote location will impact on a number of design issues including storage of consumables on site, requirements for standby equipment to maintain plant availability and requirements for spare parts. In some cases, the design of the access road itself may be a significant

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issue. A recent study involved the design of an access road running up a riverbed with associated environmental and safety issues.

2. Site topography. Facilities located on top of a hill or in a valley require careful assessment of the layout and plant arrangement. The most efficient use of the local topography must be made to ensure that the proportion of cut and fill is minimized. In general, major structures (such as crushers and mills) are located on cut, and minor structures (such as reagents and services) are located on fill. Where possible, use of gravity feed is maintained, particularly for flotation circuits.

For a flat, level site, issues of cut and fill are minimized and the constraints on layout are generally relaxed.

3. Site geotechnical conditions. The ideal site is flat, competent ground with an adequate bearing pressure and no clay. This is rarely the case and an assessment by a specialist geotechnical consultant is always part of a feasibility study. The assessment will determine what the design bearing pressure for foundations should be and assess special precautions required to prevent differential settlement of large slabs and other concrete structures.

4. Site drainage. Site drainage is a concern no matter what the climate. In tropical areas, the facilities must be designed for the daily tropical rainstorms that occur in the wet season. In the arid heart of Western Australia, the area must accommodate occasional cyclonic rainfall.

5. Transport and logistics. The majority of mine sites are self-sufficient and a regular stream of heavy vehicles is used to keep up the supply of consumables. The plant design must accommodate the frequency and form of delivery of reagents and consumables. This may include a lime silo that can accommodate a three-trailer bulk lime tanker or a large liquid caustic soda tanker or containerized liquid transporters.

6. Water sourcing. The quality and quantity of water available is a key design issue. Lack of a suitable local source of water may require a remote borefield or rainwater dam for water supply including provision for dry periods and extraordinary usage periods. A poor-quality water supply may require a water-treatment facility including anything from filtration to reverse osmosis or ion exchange.

7. Tailings storage. Design of the tailings-storage facility is the province of specialist geotechnical consultants. The site topography, drainage, catchment and geotechnical conditions together with the required storage and discharge arrangements all impact on the design. The main issue for the process plant itself is the two interfaces:

- The location and discharge arrangement for pumping tailings.
- The decant-return arrangement for recovering water and the effect of return water on the overall site water balance.

3. CRUSHING AND ORE STORAGE

The key drivers in this area of the process plant are:

- Crushing plant throughput
- Operating schedule
- Ore competence
- Ore material handling properties
- ROM and product size required
- Requirements for blending and surge capacity
- Environment.

These are discussed in more detail below.

3.1. Crushing plant throughput

The throughput has a major impact on the type of crushing plant selected for the duty. The cost of crushing plants rises in a non-linear way with capacity and a small mine is often not able to afford an expensive, automated facility. As a result, a smaller plant (<1 Mtpa) may require a single-stage primary-crushing facility operating on line with the milling circuit with minimal control. A large mine (5 Mtpa or larger) is more likely to use a large gyratory crusher with surge bin, sacrificial conveyors and coarse-ore stockpile.

As a general rule, a jaw crusher is used for plant capacity <2 Mtpa and a gyratory crusher is used for plant capacity >4 Mtpa. The area between is somewhat grey and requires individual evaluation.

Typical plant configurations for large, medium and small gold plants that demonstrates this and other points discussed later are shown in Fig. 1.

Some examples will demonstrate this point:

- A 600,000 tpa gold mine was constructed in South-East Asia. The location had low-cost labour but was in a jungle area requiring a wood-picking station. The design included a small dump hopper with retaining wall, primary jaw-crusher, wood-picking station and in-line feed to the primary mill.
- A 4 Mtpa gold mine was constructed in Africa. The design included a gyratory crusher, concrete surge hopper, sacrificial belt with tramp magnet, wood picker and stockpile feed conveyor to a coarse-ore stockpile.

3.2. Operating schedule

The key issue here is whether the crushing plant will operate 24 h per day or only part time. This influences the size of the equipment, need for standby equipment and the requirements for surge capacity between crushing and milling.

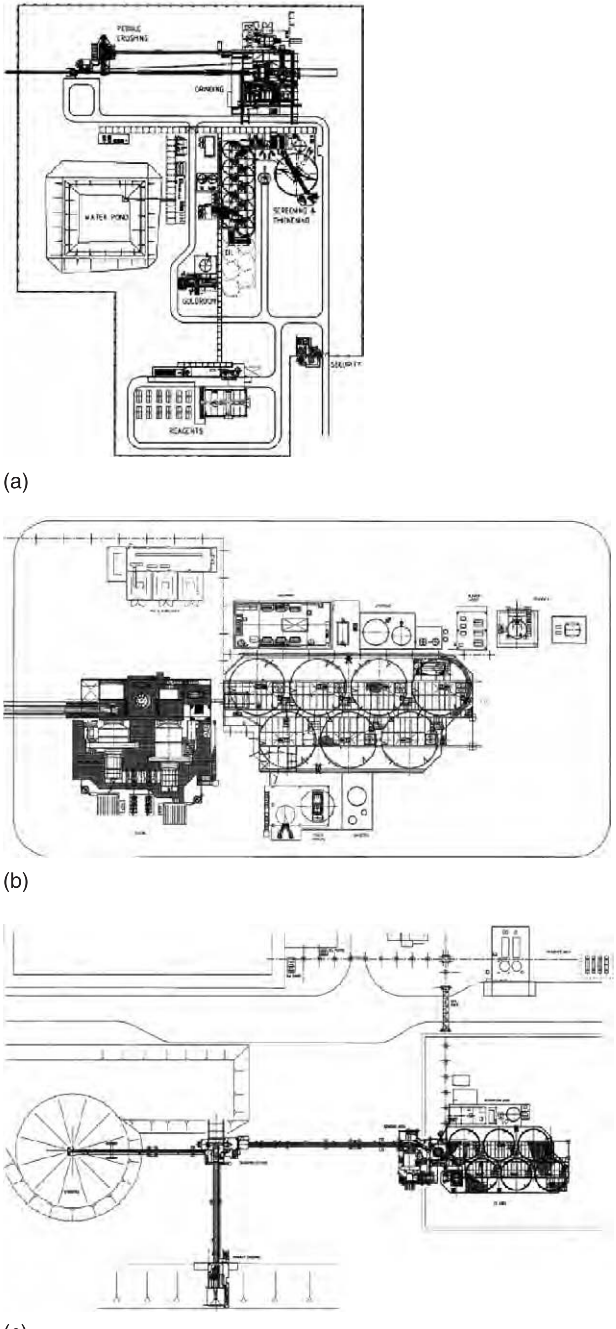

Fig. 1. Typical layouts for (a) large, (b) medium and (c) small gold plants.

Generally speaking, smaller mines operate on a 24-h schedule or as close to it as can be achieved. This avoids the overcapitalization of the crushing plant. In addition, in the event of a breakdown, a smaller plant can be kept operating with a small loader and emergency hopper.

A larger plant often operates on a dayshift-only crushing schedule with a coarse-ore stockpile in-between. The cost of downtime on a large plant is significant and this will often justify the use of a stockpile.

3.3. Ore competence

In the 1980s, many gold ores were oxide, friable and conducive to single-stage semi-autogenous grinding (SAG) mills. This situation has changed somewhat in recent years and more competent granodiorite and greywacke rock types have surfaced. These very competent rock types may require the more efficient impact breakage that can be developed in a multi-stage crushing circuit rather than the more probabilistic approach that occurs in a SAG mill.

It is impossible to generalize on the selection criteria between multi-stage crushing/ball mill and primary crush/SAG/ball mill circuit selection. A detailed comparison needs to be conducted for each circuit. Recent comparisons have indicated that the capital and operating costs for three-stage crushing can be favourable. However, the reduced circuit availability is often a deciding factor.

Once the decision has been made, some general guidelines can apply for multi-stage crushing:

- Height is the worst enemy as it adds length to conveyors, so try to keep equipment located at the lowest point on a conveyor.
- Always allow sufficient room in the feasibility study design for possible changes in equipment vendor.
- Locating the secondary and tertiary crusher on the same line as the primary crusher discharge conveyor avoids the need for transfer conveyors. This is relatively easy with small equipment but is difficult with a large plant.
- A multi-deck screen performs the scalping and final sizing role in the crushing circuit and is therefore an efficient use of space. The screen is often located at the discharge of the primary crusher conveyor. This allows the return conveyors to run parallel with the discharge conveyor back to the secondary and tertiary conveyors. This approach is fine for a small plant but is difficult to achieve in a large plant. A separate transfer station is normally required.

3.4. Ore material handling properties

Ore material properties affect the equipment selection, bin and transfer chute design. For studies, the following guidelines are used:

- For high clay-bearing or sticky ores, steep sided bins, apron feeders and steep chutes are used. Avoid the use of screens and vibrating grizzlies. Impact crushers are also favoured.
- For competent, abrasive ores belt or vibrating feeders can be used. Bins and chutes should have replaceable linings. Double-toggle jaw crushers are often favoured over single-toggle crushers for abrasive ores as the compressive action is more normal to the rock and does not lead to as high an abrasion rate.
- For ore types with a very high crushing work index, the high-pressure grinding roll can be an option. It provides a high reduction ratio and a relatively fine product. It is best suited to ores where there is a peak in ore competence in the 5–50 mm range. For gold ores, in particular, it generates a series of micro-cracks, which can enhance the ability of cyanide to permeate the ore.

3.5. ROM and product size required

The mining group normally dictates the run-of mine (ROM) size. For small facilities, this size is used to specify the minimum dimension of the crusher. A typical rule of thumb is that the ROM dimension will be no more than 80% of the minimum dimension of the crusher to avoid crusher blockages. This dimensional specification often results in a crusher that is significantly oversized in terms of capacity. In order to manage this, a static grizzly can be incorporated to divert the occasional oversize rock. This is pushed aside with the loader. For larger facilities, a gyratory crusher is usually preferred and a rock breaker is used to break down oversized rocks.

The product size is often a compromise between what is demanded by the milling circuit and what can be achieved in the crushing circuit. Typical reduction ratios and product sizes are given in Table 1.

3.6. Requirements for blending and surge capacity

Coarse or fine ore storage can be required for a number of reasons:

- A surge pile between crusher and milling circuit isolates the milling circuit from the generally lower availability achieved in crushing circuits.
- Feed to the milling circuit needs to be steady and crusher discharge can often fluctuate somewhat, particularly with smaller crushing plants.
- A stockpile can be used to blend ore from different sources. This is useful for flotation circuits where fluctuations in grade can change the mass

Table 1
Typical reduction ratios and product sizes

Crushing Stage	Reduction Ratio	Product Size (mm)
Primary jaw	4–6	100–200
Primary gyratory	4–6	150–300
Secondary cone	3–5	30–60
Tertiary cone	2–4	10–25
Tertiary HPGR	6–10	3–10

balance and circulating loads around the plant. Blending can also be done on the ROM pad.

Once the decision has been made, a number of options exist for surge capacity:

- The lowest cost alternative is to have no surge at all, but rather to have a crushing plant on line. This is workable for small-scale plant with single-stage jaw crushers as the availability of these simple plant is very high provided control over ROM size is maintained.
- The second alternative is to use a small live surge bin after the primary crusher with a secondary reclaim feeder. Crushed ore feeds this bin continuously and the bin overflows to a small conveyor feeding a dead stockpile. In the event of a primary crusher failure, the crusher loader is used to reclaim the stockpile via the surge bin, which doubles as an emergency hopper.
- For coarse ore, the next alternative is a coarse ore stockpile. Stockpiles of this type are generally 15–25% live and require a tunnel (concrete or Armco) and a number of reclaim feeders to feed the milling circuit.
- Multi-stage crushing circuits usually require surge capacity as the availability of each unit process is cumulative. A fine-ore bin is usually required. Smaller bins are usually fabricated from steel as this is cheaper. Live capacity of bins is higher than stockpiles but they also require a reclaim tunnel and feeders.

3.7. Environment

Climate can affect the design of the crushing and ore storage circuit:

- In heavy rainfall areas, open stockpiles can become quagmires and a covered system must be used. Covers are also needed over bins and chutes. This is a material-handling issue for oxide ores. However, it becomes an oxidation and acid mine drainage issue for sulfide ores.
- In dry, windy climates, dust control and prevailing wind must be considered. Dust control can range from dust suppression sprays through to full wet dust scrubbers.

- Try to avoid locating the office downwind of the ROM or coarse-ore stockpile.

4. GRINDING

For the following discussion, it has been assumed that all the necessary comminution testwork and modelling has been completed and a flowsheet agreed. This discussion relates to typical gold milling circuits consisting either of a single primary mill or a combination of AG/SAG/ball mills. This discussion does not address equipment design but rather circuit arrangement. The key design drivers in this area of the process plant are:

- Single or twin-stage
- Feed and product size
- Ore material handling properties
- Pebble management
- Power balancing
- Slurry density/viscosity
- Presence of gravity circuit
- Ball charging
- Spillage handling.

These are discussed in more detail below.

4.1. Single or twin-stage

Low-competency ores such as oxides are unlikely to have a problem with generation of pebbles. They are more likely to have a problem with slurry viscosity. For smaller plant in the 1980s, these ores were treated through a single-stage SAG mill grinding to 75 or 106 μm. This type of circuit is still straightforward in its design concept. High-competency ores or ores requiring a finer product size frequently require two stages of grinding and a number of design issues become important.

- *Mill orientation.* For smaller plant, the mills can be arranged in parallel if the products feed the same discharge hopper. This is more difficult for larger mills as the diameter of the mills drives the height required to maintain the discharge launder slope. In this situation the mills are often located at right angles. Alternatively, a transfer hopper can be used. This decision is usually based on the difference in cost and operability of each option.

- *Transfer size* from the SAG to the ball mill. Transfer size prediction is some what uncertain but has an important impact on the balance of power between the two stages of the milling circuit. For feasibility studies, a combination of modelling and benchmarking is generally used.
- *Pebble management*. This issue relates to the requirement for scatting, pebble recirculation or pebble crushing and is discussed below in section 4.4.
- *Mill drive arrangement*. Mill drives are generally located on the outside of the mill to facilitate maintenance.
- *Mill discharge arrangement*. If the SAG and ball mills feed separate pump systems this is not an issue. If the two stages feed the same pump system, the SAG mill usually drives the discharge arrangement. This is because the SAG mill is usually of larger diameter and may have a requirement for screening of pebbles to protect the mill discharge pumps and cyclones, and to facilitate pebble crushing.

4.2. Feed and product size

The main impact of feed size is on the diameter of the feed spout for the primary mill. Feed spouts are generally selected to be at least three times the diameter of the largest rock in the feed. This is not usually a problem for large throughput facilities where the largest rock may be 250 mm as the mill size will be driven by power draw. However, for small circuits (<250,000 tpa) it may be an issue. A feed size of 100 mm requires a 300 mm feed spout and this can drive the mill diameter and thus mill selection.

Product size is not usually a key driver in the typical gold plant range (63–106 μm). However, it becomes more of an issue outside this range. For coarse grind size (>150 μm) cyclone selection and operability may be an issue, particularly for small plants. In addition, care must be taken with line sizing to prevent settling, particularly for high specific gravity (SG) sulfides. For fine product sizes, dilution is necessary to achieve sharp cyclone separation. This affects cost, as it impacts on discharge hopper size, pump size and cyclone numbers.

4.3. Ore material handling properties

High-clay ores present the same problems with material handling in the milling circuit as they do in the crushing circuit. Use of steep-sided feed chutes and incorporation of belt-cleaning facilities is important at the study stage as it affects height and therefore cost.

More competent ores often require higher aspect-ratio mills and this affects the height of the overall grinding circuit. In addition, harder ores often present problems with abrasion. This can be minimized by careful design of chutes, hoppers and pipe systems.

4.4. Pebble management

More competent ores are likely to generate scats or pebbles. This needs to be accommodated in the study design as it is more expensive to retrofit if allowance has not been made upfront. Pebble management can take several forms:

- Softer ores will usually produce minor amounts of steel scats and few pebbles. This is accommodated with a chute into a bunker and is cleared on a regular basis.
- More competent ores may produce a regular stream of small pebbles. Assaying of these pebbles may indicate whether they are of low grade, in which case they can be treated in the same way as the steel scats. If the pebbles are of high grade they can be recycled directly back to the primary mill. This can be done manually by the use of a loader and emergency hopper. This usually requires a transfer conveyor to convey the pebbles to a small stockpile away from the mill discharge area. Alternatively, a conveyor system can be used to recirculate the pebbles back to the mill-feed conveyor. If a conveyor system is to be used, it is often wise to make allowance for a future pebble crusher by building in extra height.
- If the pebbles are coarse and of significant grade, a pebble crushing circuit is usually required. This will usually include
  - a discharge conveyor;
  - a primary tramp metal magnet usually suspended over the belt discharge;
  - a transfer conveyor to feed the pebble bin;
  - a secondary belt-magnet for tramp removal;
  - a small pebble bin and feeder to ensure the crusher can be choke fed; and
  - a pebble crusher located over the main mill feed conveyor.

Sizing of the pebble crusher in this application is important, as this duty is onerous. The work index of these pebbles should be tested separately to the ore to ensure that sufficient power is installed on the crusher. There is a tradeoff between efficient operation of the SAG mill (with a steady feed of crushed pebbles) and the efficient operation of the pebble crusher (choke fed).

4.5. Power balancing

Determining the transfer size in a two-stage milling circuit can be problematic. As a result, provision is often made for re-direction of some of the cyclone underflow stream to the primary mill-feed chute to increase grinding efficiency. This can impact directly on the cyclone cluster height, as a splitter box is usually required. This can be a modification to the underflow launder, or a separate splitter box.

4.6. Slurry density, viscosity and specific gravity

Oxide ores can exhibit problems with high viscosity, particularly in the milling area where slurry densities are often higher than in the rest of the gold processing circuit. This affects three areas of design:

- The slurry density for milling may need to be reduced to prevent carryover of the ball charge and to improve grinding efficiency.
- The slurry density for the cyclone feed may need to be reduced to allow a centrifugal pump to be used in this duty. Centrifugal pumps are usually limited by the yield stress of the slurry.
- The cyclone feed density may need to be reduced to provide an efficient cyclone separation, particularly at fine sizes.

Sulfide ores can exhibit high SGs (4–5 for ores with high levels of pyrite and arsenopyrite). Once again, this is particularly important in the milling area where slurry densities are often higher and particle size is coarser than in the rest of the gold processing circuit. Care must be taken with pump and piping system design and with all systems that are impacted by particle SG.

4.7. Ball charging

There are a number of methods for feeding balls into the primary and secondary mills. The method selected often depends on the size of the mill and the cost of labour as ball charging can be labour intensive. A number of methods are listed below:

- The simplest method is a *manual addition* onto the primary mill-feed conveyor. For small plants this can be as simple as adding balls from a hopper located adjacent to the mill feed conveyor via a manual arc gate. This system can be automated with a ball charger that acts on a timer to regularly dose the mill with balls.
- An alternative approach for slightly larger mills is to load balls into the *emergency feed hopper* with a front-end loader.
- For secondary mills, a *direct load-system* is required. This normally takes the form of a davit hoist located on the cyclone floor. The hoist is used for both cyclone maintenance and ball charging.
- For large mills an *automated system* is required. This may include a magnetic ball loader feeding a kibble/hoist arrangement. This system is designed to minimize the likelihood of personnel being injured. A common crane rail running over the primary and secondary mill feed chutes is required.

4.8. Presence of gravity circuit

If the gravity circuit is treating the cyclone underflow, then the main impact of the gravity circuit is on the height of the cyclone tower. In this configuration, the gravity circuit is usually fed by means of a take-off from the base of the cyclone underflow launder. This feeds a scalping screen with the oversize feeding the ball mill and the undersize forming the feed to the gravity concentrator.

If the gravity circuit is treating cyclone feed, a system for reducing gravity-circuit feed pressure may be required. This may include dummy cyclones or ceramic chokes. This does not apply where the gravity device is pressurized, although the maximum operating pressure may dictate the location of the gravity-separation device.

In either case, the tail from the gravity circuit is usually returned to the mill-discharge hopper to conserve water and the concentrate is gravitated or pumped to the gold room. This desire to gravitate to the gold room influences the gold room location, as the concentrate is dense and requires a steep launder angle to prevent sanding. In addition, pumping of gravity concentrate is difficult as the material is often coarse and of high SG.

4.9. Spillage handling

Spillage handling in the grinding circuit must deal with two situations:

- The *routine minor spillage* from pumps, hoppers, trommels and cyclones. This is cleaned up on a daily basis and does not influence the feasibility level of design.
- *Crash shutdown* of the milling circuit that requires dumping of the mill discharge hopper. This requirement drives the volume of storage under the milling area and the floor slope in the area. Floor slopes under primary mills are normally 1:12 to 1:15 for smaller plant. However, for larger plants this can be as steep as 1:8 to allow spillage to gather at a common collection point.
- For *large facilities*, manual handling is not feasible and a drive-in sump should be included for spillage handling.

5. GRAVITY CONCENTRATION

At this point it is assumed that gravity-recoverable-gold (GRG) testwork has been completed and the type of device and its location in the flowsheet has been agreed (see Chapters 4 and 13).

The main design drivers in the gravity circuit are:

- Gravity device location
- Product destination

- Water demand (quality, volume and pressure)
- Impact on water balance
- Security.

These are discussed in detail below.

5.1. Gravity device location

Gravity devices are usually placed in the milling circuit as a primary recovery device or on the leach tail as a scavenging device. The function of the device, whether for free-gold recovery or sulfide recovery, is not part of this discussion. In the milling circuit the device may be placed in a number of locations:

- Under the cyclones to treat cyclone underflow. Normal practice has been to take about 10–25% of the recirculating load and process it through the gravity circuit. Because of the coarse and dense nature of the feed, a scalping screen is normally located above the gravity device. The coarse oversize is discharged into the mill while the undersize feeds the gravity device. This type of approach is common for Knelson and Falcon Superbowl concentrators.
- On top of the mill-discharge hopper if treating cyclone feed. Treating cyclone feed is still uncommon on any other than small facilities. A bleed from the cyclone feed-line is directed into the gravity device with the tails reporting directly to the mill-discharge hopper and the concentrate advancing to the gold room. As discussed above, for non-pressurized equipment such as Knelson or Falcon concentrators, a pressure-reduction system must be included for the bleed. This may be a system of ceramic chokes or a dummy cyclone.
- For pressurized devices such as the in-line jig, the device accepts coarser feed and can accept cyclone feed pressure. However, the jig concentrate usually requires secondary processing.

5.2. Product destination

Tails from gravity circuits are normally directed to the mill-discharge hopper to conserve water. This results in a recirculating load of material passing through the cyclone cluster. As a result, the gravity device must normally be located above the mill-discharge hopper (normally in the cyclone tower).

Concentrate from a Knelson or Falcon concentrator or Kelsey jig is relatively high grade and is usually fed direct to a hopper in the secure part of the gold room. This may influence the location of the gold room.

Concentrate from an in-line pressure jig is usually coarser and lower grade (up to 20% of the feed mass) and requires secondary processing. The secondary processing may take the form of a secondary gravity device located in the milling area or an intensive leach-reactor, usually located in the gold room. In either case, the pressure in the jig is able to transfer the concentrate to its location.

5.3. Water demand (Quality, volume and pressure)

Most gravity concentrators require water for fluidizing the bed of the centrifugal units or filling the hutch of the jig. The centrifugal units have relatively fine dispersion holes so the water must be of good quality, adequate pressure, low in solids content and not likely to cause scaling. This normally dictates that the water be supplied from a raw-water source. Centrifugal units should have the water filtered (coarse and fine) and would normally include pressure monitoring and flow control. Water quality and pressure control is also important for the Kelsey jig as the water flow is introduced through small (4–6 mm) spigots.

The water-quality requirement for the in-line jig is somewhat less onerous as it does not have the fine-aperture water-dispersion system. However, water pressure is an important issue.

5.4. Impact on water balance

The majority of water in all gravity devices will report to the gravity-device tailings. In this case it means that the water will report to the mill-discharge hopper. This should be seen as part of the cyclone-feed dilution water. Ideally, the water flow should be monitored as part of the overall milling-circuit water-balance so that the cyclone overflow density can be controlled. For a milling circuit with a relatively coarse grind-size ($>106\,\mu$m), a high cyclone overflow density may be desirable to minimize tankage volume downstream. The gravity-circuit water addition may directly impact on the maximum achievable density and needs to be accounted for.

5.5. Security

Any device producing gravity gold has security implications. The emphasis on security will normally increase inversely with the average wage of the operator. A typical installation will include the following features:

- The gravity device will be located in a secure steel cage with a padlocked door.
- Concentrate will be discharged through a welded steel pipe directly into the gold room if possible.
- Water flow and pressure control is normally located outside the cage.
- The control panel for startup/shutdown is normally located outside the cage.

6. LEACHING AND ADSORPTION

For the purposes of this discussion, it is assumed that leaching and adsorption testwork is complete. Key process-design parameters for this part of the plant are:

- Leaching slurry density
- Leaching residence time
- Reagent additions (lime, cyanide, *etc.*)
- Carbon concentration
- Loaded carbon assay (Au, Ag, Cu).

These parameters are normally specified as part of the process design prior to commencing layout of the circuit and are assumed to be given. Key issues affecting the plant layout are:

- Particle size
- Slurry density/viscosity
- Requirement for leach feed thickener
- CIP or CIL
- Number of stages
- Aeration requirements
- Bypassing requirements
- Carbon movement
- Bunding requirements
- Barren carbon return
- Requirement for leach tails thickener.

These issues are described in more detail below:

6.1. Particle size

The particle size produced from grinding is not normally an issue for agitation unless it rises to greater than 80% passing 150 μm. In this situation, sanding of tanks can occur and modifications to agitator design may be required. Very fine particle-size distribution can impact on slurry viscosity and this is discussed below.

6.2. Slurry density and viscosity

The issues with slurry viscosity for high-clay ores that impact on the milling area also affect the leaching area. Three issues are worth noting for feasibility study engineering:

- Impact of viscosity on the *tank agitator design*. Typical gold slurries have an apparent viscosity in the range of 100–1000 cP. This is not normally a problem for most agitator suppliers, who specify an average shear rate of about 2.3 s^{-1}. However, high-clay slurries can have apparent viscosity measurements of up to 3000 cP. This may require a specialist agitator design. The simple solution to this is to dilute the slurry. Most slurries exhibit a kink in the viscosity/density curve between 30 and 45% solids. The design therefore needs to take this into consideration. However, at the same time, dilution of the slurry leads to an increase in tank volume to maintain residence time. A shift from 40% solids to 35% solids increases the slurry volume by about 20%.

- The ability of the slurry to pass through the *intertank screens*. The key to achieving counter-current flow of slurry and carbon in an adsorption circuit is the facility for the slurry to pass through the screen to the next stage while leaving the carbon behind. The flowrate of slurry should include both the normal slurry flow and the additional flow of slurry from carbon transfer operations. At feasibility study level, a typical intertank screen will be based on a superficial flowrate of about 60 $m^3/h/m^2$. This provides an indicative screen size for the purposes of cost estimation and drafting. However, for high-viscosity slurry, this may reduce to 30 $m^3/h/m^2$. For a large-capacity tank train, this may necessitate the use of multiple screens per stage.
- The *head loss* per stage. High-viscosity slurries develop a higher head loss per stage and therefore require a higher static head to maintain slurry flow. Maintaining a higher freeboard in the system for a *flat-deck* design can accommodate this; however, a maximum of seven tanks is normally used before introducing a step. Alternatively, the tanks can be stepped on ring beams. Steps usually employed are 75 mm for a leach tank and 100 mm for an adsorption tank. In either case, the height of the tank train increases.

6.3. Requirement for leach feed thickener

For efficient cyclone operation, dilute feed and high cyclone operating pressure usually produce a sharper cyclone split. This results in more efficient classification and avoids coarse grit in the cyclone overflow and excess fines in the underflow. As a result, the recirculating load is decreased and milling power is used more efficiently. This is particularly important for grind sizes of less than 106 μm. The leach circuit is generally operated at the maximum slurry density that does not impact on leach and adsorption efficiency and does not cause carbon to float. These two operations require different operating conditions and the leach-feed thickener provides a means of separating the two processes.

Larger gold plants have moved towards inclusion of leach-feed thickeners. Smaller plants are still divided on the issue. It generally depends on the magnitude of the difference in operating conditions between milling and leaching. The main disadvantage of the leach-feed thickener is cost, particularly for poorer-settling ore types. The advantages of the thickener are:

- It separates the milling circuit from the leach circuit in terms of operating conditions.
- It provides some limited surge capacity for minor milling-circuit breakdowns.
- It may allow the height of the cyclone tower to be reduced in some cases.
- It provides a means of separating the milling-circuit water from the leach-circuit water, thus reducing the volume of water requiring cyanide destruction.

6.4. CIP or CIL

Selecting between a CIL circuit and a leach/CIP circuit depends on a number of factors, including the following:

- *Preg-robbing* ores are generally treated in CIL circuits to avoid re-adsorption or desorption of gold onto carbonaceous material in the ore.
- CIL circuits generally have a lower capital cost for the same leach residence time, as there are fewer tanks. However, they have a higher carbon and gold inventory because the tank volume holding carbon is larger.
- Leach/CIP circuits usually achieve higher carbon loadings as the pregnant liquor tenor is higher. This allows smaller carbon inventory to be achieved.

The CIL circuit normally consists of six or seven agitated tanks of identical size arranged in a staggered formation. This allows the minimum footprint to be achieved while still providing the facility for bypassing each stage. Each tank is equipped with an agitator and intertank screen(s). The tanks are joined by launders or large-diameter piping, which allows the slurry flow to be diverted as required.

The traditional leach/CIP circuit consists of a series of leach tanks (three or more) providing the full circuit leach residence time. This is followed by a series of adsorption tanks (six or more) with a short residence time for adsorption of precious metals onto carbon. This results in two separate tank sizes with layout consequences in linking the access ways.

The traditional leach/CIP circuit has evolved into a hybrid circuit that might consist of eight identical tanks. The first three tanks provide the initial leaching and the subsequent five tanks provide further leaching and adsorption. This hybrid configuration has the advantages of higher pregnant liquor tenor, lower carbon inventory and identical tank-size.

6.5. Number of stages

The number of leach and adsorption stages is dictated by a number of issues, including:

- The choice between *CIP* and *CIL*, as described above.
- The *kinetics of leaching and adsorption*. Preliminary modelling using the Fleming model or equivalent is normally done at the feasibility study stage. Given the leach feed-grade, target loaded-carbon and tails-solution grades, this will dictate the number of stages required while still managing the gold and carbon inventory.
- Consideration of potential *bypass conditions*.

6.6. Aeration requirements

The oxygen demand of different ore types varies widely. Oxygen is generally introduced in two ways:

- *Low-pressure blowers* provide aeration, generally down the agitator shaft or via sparges under the lower agitator impeller. This is suitable for low to medium oxygen-demand ores and is generally limited to one tank volume per hour.
- *Cryogenic or pressure-swing adsorption facilities* provide oxygen that is directly sparged into the slurry, through the side of the tank or down the agitator shaft. The sparge is generally located just below the agitator. This is used for high oxygen-demand ores often containing active sulfides.

6.7. Bypassing requirements

The tank train is generally arranged to allow each tank to be bypassed. This can be done using launders running over the top of the tanks (for the Kambalda type screens) or via a dart valve located in the discharge box. Screen discharge can be hard piped from tank to tank; however, this may lead to flooding if the density of the slurry in the two tanks varies. Selection of seven or more tanks allows one tank to be bypassed at a time while still maintaining the minimum of six tanks to prevent short-circuiting of pulp.

6.8. Carbon movement

The loaded-carbon grade and the precious-metal extraction efficiencies dictate the rate of carbon movement required. Carbon is generally advanced by either airlift (for smaller plants) or by recessed impeller pumps. The plant design must take into consideration the impact of the return slurry flow from carbon advance on the intertank screen capacity. For average-grade gold plants this is not an issue. However, for ore with a high silver grade, the carbon movement may be significant. This can lead to large slurry flows coming from carbon movement. In this situation, separate carbon-transfer screens may be included to allow the slurry to return to the tank from where it came while still allowing the carbon to advance.

6.9. Bunding requirements

Concrete bunding around the leach/adsorption tank train is designed for access and spillage management rather than total containment. If total containment is required it is generally achieved using a separate containment pond.

6.10. Barren carbon return

Following elution, barren carbon is either returned directly to the adsorption circuit or is regenerated. The trend today is towards a horizontal regeneration-kiln. For smaller plant this is located on top of the CIL tanks. This allows the barren carbon to gravitate directly into the requisite adsorption tank after screening and avoids the need for a separate support structure. For larger facilities, the regeneration kiln and associated feed hopper can be substantial and may provide significant structural loads. In this circumstance, the regeneration kiln is located at a lower level and the regenerated carbon is hydraulically transported to a screen on top of the adsorption tanks.

6.11. Leach tails thickener

A leach tails thickener is generally included if water recovery or cyanide recovery is critical to project economics. This may be the case where water is in short supply or a start-up water supply is not available.

7. CYANIDE DETOXIFICATION AND TAILINGS DISPOSAL

More and more facilities are relying on a cyanide detoxification step prior to tailings disposal. This chapter does not discuss the pros and cons of the various processes used for cyanide destruction or recovery (see Chapters 28 and 29). Rather it briefly describes the key issues that impact on overall plant design. These issues include:

- Residence time
- Number of stages in the process
- Aeration and agitation requirements
- Materials of construction
- Tailings pumping.

7.1. Residence time

The residence time for these processes varies hugely. It can be as low as 1 min and be conducted in the tails disposal line via an in-line mixer; or it can be 2 h, in a multi-stage tank train.

The residence time required for the process dictates the size and number of tanks required. As many of these processes are gravity fed from the leach/adsorption circuit, the size of tank is important. In the worst case, the discharge from the adsorption circuit will come from the second-last tank (if in bypass) and will feed a carbon safety-screen before discharging into the detoxification tank. A significant height loss is involved in this transfer and this may dictate the choice between one and two tanks, regardless of process requirements.

7.2. Number of stages in the process

The processes requiring longer residence time are often specified in two stages. These are usually two adjacent tanks with an overflow feed-system so that little static head is lost between the tanks. Increasing the number of stages increases the cost of the facility as there is more equipment; however, it does assist with process control and prevents short-circuiting of process slurry.

7.3. Aeration and agitation requirements

For some of the detoxification processes, the aeration demand is very high. In addition, for larger tanks, the discharge pressure required can be higher than is normal for a typical low-pressure blower. Up to 100 kPa a conventional blower can be used. Above that, a multi-stage centrifugal blower should be contemplated.

In this highly aerated environment, the agitator must be specified to cope with this arduous duty. As the duty relates to gas dispersion/dissolution rather than suspension of solids, the power demand is considerably higher than for an equivalent-sized CIL tank. The design of impeller must change to a *high solidity* type to prevent short-circuiting of gases to the surface of the tank.

7.4. Materials of construction

Even though the pH is normally mildly acidic to alkaline, tanks for this duty are normally specified with rubber-lined steel as the wear can be high.

7.5. Tailings pumping

Tailings pumping is a whole subject in itself and should be handled by a specialist consultant if the duty is in any way unconventional. A few issues to look out for include the following:

- If the tails pump discharge head is higher than 60 m of slurry then multi-stage pumping will probably be required.

- High-viscosity ores will increase the demands on the pump system and may require dilution.
- Caution should be exercised with coarse particles in the tails system as this may lead to sanding.
- A system for positive flushing of the tails line with process water after plant shutdown should always be included.

8. ELUTION AND GOLD ROOM

At this point, it is assumed that the size and type of elution circuit has been selected for the process plant. The selection of type of circuit is complex and may be based on a number of issues, including capital cost, cycle time, water quality or other considerations. While the type and size of the elution circuit is an important part of the feasibility assessment for the project, the capital cost of this area of the plant is a relatively small part of the overall project cost. It generally ranges from 5 to 10% of the treatment plant cost. Design considerations for this area include the following:

- Type of elution circuit
- One or two columns
- Column location
- Degree of automation
- Location of gold room
- Complexity of gold-room operations
- Security.

8.1. Type of elution circuit

The more common types of elution circuit include:

- *Atmospheric or pressure Zadra circuit*. The key issue here is the continuous nature of the strip/electrowinning process and the need to ensure that the discharge from the column can feed the electrowinning cell and thereafter the eluate tank. The Zadra circuit can generally accept poorer-quality water although this may extend elution cycle time.
- *AARL circuit*. The key issue with this type of circuit relates to water quality and automation of the process. AARL circuits generally operate best where the water contains less than 500 mg/L total dissolved solids and the dissolved salts are unlikely to cause scaling. Where higher likelihood of scaling is anticipated, a regular cleaning schedule with sulfamic acid should be anticipated. The level of automation in the AARL circuit is generally higher to ensure the correct sequence of heat-up, soak, elution and cool-down

stages. The separation of electrowinning and elution makes this circuit more suited to fast cycle times.
- *Split Anglo circuit*. The issues here are similar to the straight Anglo circuit although with the added complication of having two eluate streams. This circuit is favoured where there is a limitation in water quantity.
- *Integrated pressure strip (IPS)*. The IPS system is a packaged plant where both elution and electrowinning operate under pressure.

8.1.1. One or two columns

The key issues here are elution cycle time and elution temperature. A single acid wash/elution column can be used if there is sufficient capacity in the system to accommodate the extra time required for acid wash, rinse and carbon transfer as well as the normal elution cycle. This can be appropriate for lower-temperature Zadra circuits that do not need to operate every day. If the elution temperature is below 110°C, a single rubber-lined column can be used for both acid washing and elution. Above this temperature, two separate vessels are required. Typical Zadra cycle time is about 16 h.

If an elution circuit with a relatively short cycle time, such as an AARL circuit is used, then two separate columns are required. One of the advantages of the AARL circuit is the ability to complete the elution cycle in 6–8 h, allowing two cycles to be completed in a day. If a single column is used, then this cycle time can be extended by 2–3 h, making multiple strips more difficult to achieve in a single day.

8.1.2. Column location

The location of the acid-wash column is normally driven by the location of the loaded-carbon screen and the ability to gravitate loaded carbon into the column. This may be dictated by whether the circuit is CIL, CIP or a hybrid. For a Zadra circuit, it may also be influenced by the location of the gold room in the milling circuit, which can push the stripping circuit further down the tank train. Favoured locations are:

- Between milling and the first tank (for CIL) located under the cyclone tower for smaller throughput facilities and where a gravity circuit is included.
- Halfway down the train nestled between Tanks 3 and 4 (for hybrid circuits).
- In a line parallel to the tank train incorporating gold room, eluate tanks and columns. This can impact on constructability.
- In a separate independent compound if gravity concentrate processing is not an issue.

8.1.3. Degree of automation

Elution circuits can be fully automated or fully manual. As a general rule, Anglo circuits are usually automated and controlled by a stand-alone PLC. Zadra circuits can be automated but are frequently fully manual as there are fewer valve changes to make and elution occurs over a longer time.

8.2. Gold room

8.2.1. Location of gold room

The location of the gold room is dictated by a number of competing factors:

- If there is a gravity circuit, the gold room is normally close by to allow the concentrate to gravitate. This means it is either adjacent or under the milling area.
- If there is no gravity circuit its location is dictated by proximity to the elution column as described above. In the case of a Zadra circuit where the elution and electrowinning operations are inextricably linked, this is a requirement. This is less so for the AARL circuit.
- In some more remote overseas operations, security is a major concern and the gold room is placed within sight of the offices/security complex in a separate compound.

8.2.2. Complexity of gold room operations

Gold room operations can be as simple as a single electrowinning cell and eluate tank, drying oven and smelting furnace. Or they can incorporate gravity-concentrate tabling, separate concentrate leaching, multiple electrowinning cells, cell-mud handling and filtration and large-scale smelting operations. The complexity of the operation generally dictates the layout. The following issues are typically taken into account:

- Occupational health is paramount and adequate fume extraction and shower facilities must be provided.
- Gravity flow is used wherever possible with electrowinning cells located on a mezzanine floor.
- All hoppers and wash vessels must encourage flow, because cell mud is a high SG material.
- Operator access to key control points such as electrowinning rectifiers must be maintained external to the gold room for security.
- Adequate wash-down and silt trap facilities must be provided.
- The building must be secure.

8.2.3. Security

The level of security attached to a facility is site specific and is driven by a number of considerations:

- The economic development of the country.
- The level of institutionalized gold theft.
- Client preference.

At the lowest level, the gold-room security will include motion sensors, closed-circuit television (CCTV) cameras and a locked door.

At the highest level it will include all the above together with a separate perimeter fence with CCTV, *in situ* guards and body searches.

9. FLOTATION

For sulfide ores (usually pyrite or arsenopyrite based), flotation is often the first step after grinding to recover a gold-rich concentrate (see Chapter 14 for more details). The tail from flotation may advance to a CIL circuit while the concentrate is usually subjected to fine grinding or oxidation prior to leaching and gold recovery. This section provides some general comments on the key layout issues in feasibility-study design for the flotation section. These issues include:

- Flotation slurry density
- Residence time
- Circuit configuration
- Product destination
- Wear and corrosion
- Froth tenacity
- Presence of an OSA system.

9.1. Flotation slurry density

Flotation feed-density is often more dilute than the density of slurry exiting the grinding circuit. This is usually accommodated with a conditioning tank. At this point, dilution water and flotation reagents are added. The conditioning tank is normally located ahead of the first float cell so that the feed can flow by gravity into the first float cell.

9.2. Residence time

Residence time is one of the parameters used to specify the number and size of flotation cells in the circuit. For a feasibility-study design, the laboratory residence time will be scaled up by between 1.5 and 2.5 to allow for less-efficient mixing in a full-scale facility. This scale-up factor reduces somewhat if pilot flotation results are used. An allowance for air hold-up is also normally made. This will vary between 10 and 25% of volume, depending on the application. For each stage of the process (roughing, cleaning, *etc.*) a total installed volume is calculated.

The number of cells is determined based on experience with cells suited to that size of plant. For example, a flotation plant requiring 120 m^3 of total rougher capacity could use cells of 4, 8, 10, 16, 20 or 30 m^3 capacity. The resultant number of cells would vary from 4 to 30. The roughing duty in this example may be open circuit to tail. Any material that short circuits may not receive a second opportunity for flotation. Experience with continuous stirred-tank reactors suggests that six cells in series provides little or no short-circuiting of feed. Based on this experience, either 16 m^3 trough cells or 20 m^3 tank cells could be selected. Further checks on carrying capacity and launder capacity are also usually completed.

9.3. Circuit configuration

Circuit configuration refers to the arrangement of roughing, scavenging and cleaning stages. Simple pyrite flotation circuits usually include roughing, scavenging and one or two stages of cleaning. The key issue here is the maximization of gravity flow. Cleaning stages are often arranged in line ahead of the rougher and scavenger to allow the tails streams to gravity feed through cleaner, secondary cleaner and primary rougher/scavenger. Intermediate concentrates are then pumped counter-current to this gravity flow. This arrangement works for limited cleaning stages, but cannot be maintained for large-scale facilities as the height of equipment becomes a cost issue.

9.4. Product destination

Most flotation circuits are a trade-off between flexibility and cost. One of the contributors to flexibility is the ability to route concentrate streams to a number of different destinations. In particular, the first cells from a particular bank are fast-floating and often higher-grade material. The option to skip a stage of cleaning is often included in a float-circuit design as this reduces the circulating load and the potential increased tail grade. This can be achieved by raising equipment high enough to allow launders to flow to one of the two destinations. Alternatively, cleaning stages are arranged in parallel with concentrate pumps situated centrally to provide multiple options.

9.5. Wear and corrosion

A substantial part of the cost of a flotation cell relates to its surface protection. For active and abrasive pyrite, rubber lining of flotation cells is common in long-life facilities. This is particularly the case if the grind size is coarse. If the feed material is relatively fine, non-abrasive and at high pH, an epoxy paint system may be adequate.

9.6. Froth tenacity

If pilot work has been completed, it always pays to observe the ability of the froth to breakdown in launders and pump hoppers. While the majority of froths break down easily, it may be necessary to modify hoppers and launders to accommodate tenacious froths.

9.7. Presence of an on-stream analyser (OSA) system

The location of an OSA system needs to be carefully considered. There are two general philosophies:

- Locate the OSA system high enough to gravitate the return streams and ensure that all feed streams are pump fed. This is often favoured for complex circuits where there are many return destinations.
- Locate the OSA system low enough to gravitate all the feed streams and have a single, common pump return. This is often favoured for simpler float circuits where all streams return to one point.

The volume of sample required by the OSA system may dictate whether a dedicated transfer pump is required.

10. REFRACTORY ORE PROCESSING

The following sections provide general comments that are intended to flag issues requiring some consideration during the study process. Although there are a number of refractory ore processes available, only three are discussed below.

10.1. Bio-oxidation

The significant issues in bio-oxidation (see also Chapter 16) are:

- *Pilot testwork.* To provide a reliable basis for design, the process should be piloted by a reputable laboratory. This will provide the key data to allow the bio-oxidation and downstream processes to be designed with confidence. In some instances technology providers will offer process guarantees with only bench-scale testing; however, this opportunity is rare.
- *Slurry density and residence time.* This is dictated by testwork and is generally of the order of 20% solids and 120 h. The first three tanks are generally arranged in parallel to prevent washout of the bacterial culture. Thereafter, three tanks are arranged in series.

- *Cooling and heating*. Oxidation of sulfur generates considerable heat. This heat must be dissipated to allow the bacteria to survive at a stable temperature of around 40°C. This heat dissipation is normally achieved by running cooling water through a series of coils located in the oxidation tanks. The resultant hot water is then passed through evaporative coolers before being recirculated. This cooling system is a substantial consumer of power and is very site dependent (ambient temperature, altitude, humidity, *etc*.).
- *Air requirements*. Bio-oxidation requires considerable volumes of air supplied by low-pressure blowers. This can also contribute significantly to power demand.
- *Water quality and balance*. The water system for the bio-oxidation facility must be kept separate from the main CIL water system because the introduction of cyanide or thiocyanate will kill the bacteria. The water used for feed dilution must be recovered if possible to minimize the introduction of fresh water. Other deleterious elements in the water include chlorides, which impact on materials of construction and at levels above 1,000 mg/L can kill bacteria.
- *Security of power*. Loss of power to the area will lead to a failure of aeration, cooling and agitation. This will cause the bacteria to become dormant or die.
- *Materials of construction*. The oxidation environment is acidic and highly agitated. This is a difficult environment for material selection. Generally, tanks are either stainless steel or rubber-lined steel.
- *Acid and limestone supply* for pH management. The bacteria used for oxidation thrive in an acidic pH environment (1.5–2). The pH of the slurry will be affected by the natural buffering ability of the ore. It may be necessary to add acid or limestone to manage the pH and to neutralize the product. This can be a significant cost driver in remote sites where these pH modifiers may need to be transported a considerable distance.
- *Arsenic stabilization*. Arsenic that is solubilized by the process is usually stabilized into a ferric-arsenate precipitate to prevent release to the environment. Most pyritic concentrates contain sufficient iron (greater than 3:1 molar ratio) to stabilize the arsenic in the neutralized residues.

10.2. Pressure oxidation

Design of a pressure oxidation facility is a specialist process (see also Chapter 15). There are a number of issues to be considered during the design process:

- *Pilot testwork*. To provide a reliable basis for design, the process should be piloted by a reputable laboratory. This will provide the key data to allow the process to be designed with enough confidence. The cost of piloting can be large, however, and in small projects the cost may be offset by accepting bench-scale tests for the design and using the cost of piloting as a project contingency.

- *Degree of oxidation*. Greater than 95% sulfur oxidation is normally targeted and is dependent on cyanidation performance and gold-recovery behaviour.
- *Temperature and pressure*. Pressure oxidation circuits operate at severe conditions of temperature and pressure. This can range from 180 to 220°C and 30 to 40 bar in gold circuits. The optimum conditions are normally specified based on the pilot testwork and will influence autoclave design, materials of construction, feed pump and letdown equipment design and consequently capital cost.
- *Residence time*. This is normally determined by modelling of the batch testwork with due consideration of the number of compartments in the autoclave and possible short-circuiting.
- *Materials of construction*. Acid brick linings are common, together with significant use of high-quality stainless steels and titanium alloys.
- *Control*. Sophisticated controls with integral safety systems are required for effective process control in pressurized systems.
- *Oxygen supply*. Depending on the oxygen demand, a pressure swing adsorption (PSA) or cryogenic oxygen supply is required.

10.3. Roasting

Roasting of whole ores or concentrates has become less popular due to environmental concerns with sulfur dioxide and greenhouse gas emissions and the disposal of arsenic trioxide from arsenopyrite concentrates. Design of a roasting facility is a specialist area and design considerations include sulfur oxidation conditions, temperature, product recirculation, product quenching, gas handling and scrubbing (see also Chapters 17 and 18). For arsenic-bearing ores, handling of arsenic trioxide in the gas stream can be a difficult issue.

11. SERVICES AND UTILITIES

11.1. Reagents

A few general comments on reagent systems are appropriate:

- *Bulk lime* is generally added dry onto feed conveyors via a silo and rotary valve/tube feeder for conventional gold plants. A lime slurry is used to adjust the pH down the leach train. This is normally mixed to 20% solids and pumped via a ring main. The easiest control system for the slurry is a solenoid valve operating off a timer. Lime can be sourced as quicklime or hydrated lime depending on the economics of the location.

- *Cyanide* mixing and distribution depends somewhat on location. Within about 600 km of a major centre, liquid cyanide is transported cost-effectively to on-site bulk storage tankers. This removes the need for on-site mixing with all its attendant safety issues. The cyanide solution can then be pumped direct from the bulk tanker to the leach and elution circuits. In more remote locations, mixing from briquettes is still required.
- *Caustic soda and acids* may also be transported in bulk tankers and stored in a similar way to the cyanide solution for large operations. For small operations, isotainers and bulk boxes are still an effective alternative.
- In terms of *layout*, normal rules of storage apply for hazardous chemicals with acids and alkalis separated and fuel and oxidants being separated.

11.2. Power

The main feasibility study issue to consider is whether the power is from the grid or by on-site generation.

- If from the *grid*, defining the battery limit from the power supplier is a key issue along with the quality and security of supply. The battery limit will normally be the feed to the high voltage substation. This substation should be located near the large power demand area. In areas where power interruptions are frequent and extended, backup generators for essential services should be provided.
- If the power is *on-site* generated then location is an issue. The power station must be located close to the large power demand centres (normally milling) but as far as is practical from the dust generating areas in the crushing plant. It must have access for bulk fuel delivery. An appropriate balance of duty and standby engines must be selected with the ability to handle start-up, peak and average loads.

11.3. Water

There are at least three water systems on a typical mine site:

- *Potable water*. If sourced from a borefield then treatment through a sterilizing system is a consideration. If it is to be used for elution (in an AARL circuit) then quantity and storage are an issue.
- *Raw water*. If sourced from a catchment dam then seasonal catchment must be considered. If sourced from a borefield then remote power, access and pipeline design are issues. After this, the size and type of storage needs to be considered. This water source generally forms the makeup supply as well as feeding the firewater system. Steel tanks are generally used to store up to 500 m^3, with dams used for over 1,000 m^3.

- *Process water*. This is generally sourced either by thickening tailings or by return from the tails dam. The main use of process water is in the grinding area. Storage is normally in a dam although spare CIL tanks have also been used.

11.4. Air/oxygen

Air is normally supplied in two forms:

- as *low-pressure* air for aeration in the leach and cyanide destruction circuits. The key consideration here is the static head required for aeration as this will dictate the type of blower to be used, and
- as *high-pressure* compressed air for instruments, air tools, mill clutches, airlifts *etc*. Compressor packages are normally supplied complete with their own control package for loading up on demand.

Oxygen can be supplied by two methods:

- *Cryogenic* oxygen supply – normally for facilities consuming more than 30–50 tpd.
- *Pressure swing adsorption* (PSA) – normally for smaller facilities (<20 tpd).

11.5. Fuel/diesel/gas

The decision on which fuel to use is generally driven by location. Gas is usually preferred if the gas supply is relatively close. Diesel is the standard for remote sites as it can be used for mine vehicles, power stations and process-plant equipment (heaters, kilns, smelters, *etc*.). In addition, in Australia, diesel attracts a federal rebate that makes it more attractive.

Diesel storage facilities are generally designed to include 110% containment using an earth bund. Gas storage generally requires full fencing, deluge system and a significant separation distance from other facilities.

12. SPECIAL ISSUES FOR LARGE FACILITIES

A number of issues need to be addressed when dealing with large-capacity process facilities:

- Because of the large quantities involved, structural design of large concrete structures should be completed at a preliminary level. This includes crushing chambers, reclaim vault and mill foundations.
- Major steel structures should also be designed to ensure that major members are sized and steel quantities are appropriate.

- Large facilities include large-bore pipe that generally consumes significant space on pipe racks and bends. Preliminary pipe runs for all large-bore pipe should be completed.

13. CONSTRUCTABILITY

The feasibility design must also consider the overarching issue of constructability. This involves a number of issues, including the following:

- Is there a safe access onto the site for equipment and materials
- Is there a lay-down space for equipment and materials
- Is the largest lift feasible by available equipment
- Does the design allow for access by large-capacity cranes
- Does the layout allow for construction by a number of contractors at the same time.

14. PITFALLS IN FEASIBILITY DESIGN

Issues that the authors have had experience with but which is assuredly not a comprehensive list are as follows:

- The availability of the entire process plant is dependant on the reliability of the least reliable item of equipment. *Redundancy of equipment* should receive careful consideration.
- Spillage during upset operation may result in sections of the plant becoming inoperable or unmaintainable and impacting on plant availability. *Managing excessive spillage* should be built into the design layout.
- *Capital costs* are usually not significantly reduced by selecting cheaper equipment or removing redundancy. Operability and availability are both usually compromised in addition, leading to increased operating costs.
- *Surge capacity* between unit operations should receive careful consideration. Unplanned equipment outages should not immediately impact on preceding or subsequent processing stages. Sufficient time to bring redundant equipment on line or to fix the problem should be allowed.
- Do not allow the overwhelming desire to ensure that the project proceeds override *sound engineering judgement and the proper selection of equipment*. Conservative design principles should generally not be questioned.

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I.2 *Commissioning*

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Chapter 7

Commissioning

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1. INTRODUCTION

This chapter addresses the commissioning activities that bring a gold plant from the construction phase to routine plant operation. These activities should be initiated early in the engineering and design phase to ensure that construction is scheduled such that commissioning occurs in a safe, timely and cost-effective manner.

Commissioning includes all activities relating to installation testing, no-load testing, systems checks, water commissioning, ore commissioning, performance trials and early gold plant operation. This process may be facilitated in numerous ways dependent on the nature of the project, the nature of the contractual arrangements between the owner, managing contractor and construction contractors and the size of the project. For example, the managing contractor for a lump sum turn-key project may be responsible for all phases of commissioning to final completion, whereas the managing contractor of a complex multi-contract project may only be required to bring the project to mechanical completion and then hand over to the owner for ore commissioning.

Irrespective of the responsibilities, commissioning programmes require careful planning, effective communication and detailed reporting. Managing the expectations of all parties, particularly when cost pressures exist on the project, is one of the first activities during the lead up to ore commissioning. Effective communication throughout the project with engineering, construction management, contractors, vendors and owner's representatives is paramount. Failure to recognize a common goal retards progress to

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completion. Unsuccessful commissioning can significantly impact on project cash flow and early profitability.

The commissioning programme should be planned to ensure that safety hazards are identified and controlled, deadlines are achievable, manning is available, costs are contained, and plant and equipment are protected.

Detailed reporting of commissioning activities is critical in providing a reference document, and for the possible later resolution of conflict regarding contractor's, manager's, vendor's or owner's interpretation of achievements.

2. AN OVERVIEW

The commissioning process should be initiated during the engineering phase of a gold project. For large, complex projects, commissioning planning may commence during project feasibility study assessment with dedicated personnel, while for smaller projects, commissioning may be considered in parallel with detailed process and engineering design by the design team.

Key factors that impact on the commissioning process are:

- Size of project,
- Project complexity, for example, nature and number of unit processes,
- Implementation strategy and contracting structure,
- Owner's project and commissioning experience.

The commissioning strategy and plan must be reflected in all contracts for equipment and supply of services. This requires the preparation of a commissioning plan and a technical specification that are referenced in all contracts. This avoids the potential for later conflict regarding allocation of responsibilities and assists in cost control.

The commissioning phase can significantly affect early project cash flow. Poor commissioning planning can lead to ongoing project difficulties, while a rapid commissioning allows operational personnel to focus on project optimization and long-term planning. Understanding the design contingencies and associated risk profile flowing from the design criteria and project expectations arising from contractual agreements is critical. A short, smooth commissioning and start-up can dramatically enhance project economics.

Commissioning planning may be combined with consideration of process operability and equipment maintenance issues. This continues through the procurement and construction phases with planning and scheduling of installation testing, assisting with detailing contractor tasking and determination of vendor start-up support requirements. Ongoing interaction with procurement and construction management ensures that critical services and plant ancillaries, required for pre-operational testing, are complete prior to the main plant.

Commissioning usually becomes an intense process with tight deadlines as the plant construction nears completion. Delays in commissioning impact on the owner's cash flow. Effective communication with all the project participants, including owner's representatives, vendors, contractors and the construction team, requires extensive planning and clear definition of procedures, cost control and reporting requirements.

Commissioning can be divided into a number of phases:

- the *definition and planning* phase, co-incident with engineering, procurement and construction,
- *installation testing* phase, including witnessing of critical installation tests and undertaking of mechanical and electrical functional checks;
- *systems checks* and no-load operation of equipment;
- *water testing* of systems, and *preliminary tuning* of control systems;
- *preliminary operation* of the plant with ore and process fluids;
- any necessary *modification* of the plant to achieve design objectives;
- completion of *process tests*, if required, to demonstrate any warranted operating conditions, and
- *handover* to the owner and early plant operation.

The effectiveness of each of the above phases is cumulative, with the successful outcome of each phase reliant on the success of preceding phases.

Selected definitions of the various terms used in this chapter are given in Section 9.

3. IMPACT OF PROJECT SIZE, CONTRACTING STRATEGY AND PROCESS COMPLEXITY

Project size, contracting strategy and process complexity are the principal determinants of the most appropriate commissioning strategy. Gold plants can vary from small (150 kt/a or smaller) CIL-based plants to large and complex plants treating refractory ores that may include stages of concentration (by gravity or flotation), concentrate treatment (pressure oxidation, bio-oxidation or roasting), gold recovery by CIL or resin technology, cyanide recovery or destruction, gold recovery, tailings disposal and associated services.

3.1. Contracting strategy

Three examples of prime contract type and their impact on commissioning activities are discussed below.

3.1.1. *Lump sum turn key projects*

Lump Sum Turn Key (LSTK) contracts are often used for smaller projects, or by junior resource companies with limited operating or financial backing. LSTK contracts require that a contractor supply an operating plant to the owner. Such contracts are often promoted to reduce the risk to the financier by transferring risk to the contractor. The competitive nature of these contracts can lead to cost minimization measures that can influence plant design, the commissioning methodology and commissioning outcomes. The contractor is obligated to provide a plant that meets pre-determined performance criteria as specified in a performance warranty. The contractor designs, engineers, procures equipment, constructs and commissions the plant in the most cost-effective manner, nominally with minimal owner input, within the provisions of the contract. In reality, attempts are made in all of these phases to meet Owner preferences, often resulting in contractual variations and the owner's personnel commonly assist in the commissioning of the plant.

In Australia, LSTK contracts have typically been used for lower budget, modest capacity gold plants. The design and project cost are based on the contractor's experience with similar projects and in some cases *off-the-shelf* process plant packages may be available.

The level of documentation of installation testing and other pre-commissioning testing activities is often not driven by the owner, as the degree of commissioning detail in the prime contract is often minimal. This leads to a minimalist approach to the documentation of testing, resulting in reduced cost to the project and a faster pre-commissioning period, particularly with technically simple plants (the technical simplicity may come through experience).

Installation testing may be undertaken by the design and construction team with minimal additional resources due to the modest size of the typical Australian LSTK job and the modest resources available to the project.

LSTK projects are nearly always accompanied by process warranty provisions where the contractor is required to demonstrate that the plant is 'fit for purpose'. Performance warranties are discussed in Section 7.

3.1.2. *EPC contracts*

Engineering, procurement and construction (EPC) contracts typically occur with identifiable unit operations capable of operating as separate entities. EPC contracts may be minor, as in a water-storage system, or a part of the process plant, such as a primary crushing plant.

All installation and pre-commissioning activities, up to and including systems checks and no-load commissioning are completed by the EPC contractor. In most cases, the contract will have performance warranty provisions to ensure the facility is 'fit for purpose'.

The managing contractor or owner usually manages water and ore commissioning and closely supervises critical pre-commissioning activities, including the witnessing of selected installation tests, all system checks and no-load testing.

The performance of and documentation for pre-commissioning and commissioning activities required of the EPC contractor are prescribed by the owner's or managing contractor's technical specification referenced in the contract. It is critical that the managing contractor ensures that the EPC contractor is aware of the obligations to pre-commissioning and commissioning at the time of contract award. This includes definition of tasks to be completed under any lump sum component and activities to be conducted on a reimbursable basis.

3.1.3. EPCM contracts

Engineering, procurement and construction management (EPCM) contracts take a number of forms with varying contents of direct hire and contract management. The EPCM contract may include either or both of the above contract types as sub-contracts to the prime contract.

The EPCM contractor (managing contractor) is responsible for all activities on the site. As such, responsibilities include ensuring that the various sub-contractors abide by the standards and specifications set out for the project and that the owner's requirements are met in all aspects of commissioning.

3.2. Project complexity

The technical complexity of a project, particularly when associated with a brownfields project, not only necessitates that the commissioning team has access to the requisite technical skills but is also able to communicate knowledge to the construction, testing and operations teams. Greater process complexity may increase the resources and time required to commission the plant. Each unit process should be commissioned in a logical manner as construction is completed and feed materials become available.

The complexity of commissioning increases with the number of parties involved with the project and, therefore, increases with contractual complexity from LSTK to EPC to EPCM. If the project involves expansion of an operating plant, or brownfields project, an added order of complexity and level of project planning is required, due to the requirement to schedule *cut-ins* to an operating plant and commissioning of new equipment alongside operating plant.

The commissioning of new technology in a brownfields site is perhaps the most challenging commissioning activity. Giraudo *et al.* (2000) describe the commissioning of the pressure oxidation (POX) plant at Macraes Gold Mine in 1999. This particular project was commissioned to design capacity in a matter of days, indicating that process novelty should not be a driving factor in commissioning duration. Poor planning and/or poor design are usually the key contributors to less successful project commissioning outcomes.

3.3. Project size

Large projects are typically associated with more complex contracting strategies, but not necessarily greater flowsheet complexity. The complexity of the contracting strategy and the increased focus on key items of equipment, such as large grinding mills, elevates the manning requirements. Larger throughputs and associated larger equipment does lead to increased complexity in service equipment such as lubrication, cooling and control systems. Ring motors on large semi-autogenous grinding (SAG) mills require significant installation testing and commissioning effort. The 20 MW drive for a large Australian gold/copper project with a capital cost of approximately A$295 M in 1998, took three technicians over 6 weeks to test and commission and the total vendor cost (installation and commissioning) for the 20 MW ring motor alone exceeded $1 M.

4. COMMISSIONING PLANNING

4.1. When does commissioning start?

Commissioning is a demanding period during which pressures can be brought to bear by the owner on contractors to maximize cash flow and profit. Commissioning can be characterized by a succession of crises if preparation and communication of the commissioning plan is not effectively completed during the engineering and construction phase of the project.

Planning must commence in parallel with detailed design and be integrated with the technical, maintenance and operating review process. Planning and scheduling aim at ensuring a common goal, and focus on a logical and sequential approach to the plant commissioning phase. The planning process includes the early identification of key personnel who will ensure the operability of the plant and the sequential construction of services as required prior to the main plant pre-commissioning activities.

4.2. The planning process

A detailed discussion of the planning process, roles and responsibilities, scheduling and turnover package preparation is presented by Churchill and Lane (1997). Input is sought from process, mechanical, electrical, instrumentation and distributed control system (DCS) engineering personnel, together with contract managers, construction managers and superintendents, vendor engineers and the owner's team.

Preliminary commissioning plans are developed and continually reassessed during construction. The level of detail is dependant on the project and may vary from a bar chart of general process areas to a detailed schedule based on engineering equipment lists. The Ok Tedi Gold Project Pre-Operational Test Programme involved the scheduling and conduct of approximately 3,000 individual tests (Churchill, 1986).

As software packages improve, the tendency towards more detailed sequencing of tasks increases. The Telfer Project commissioning plan is based entirely on an electronic database that is fully integrated with the engineering databases and reports on all activities (Fleay, 2004). Sequence scheduling is typically conducted on three levels:

- *project commissioning schedule* by unit operation, area, system and sub-system;
- *three-week rolling schedules* as sub-sets of the project schedule detailing the pre-commissioning activities to an equipment level, or detailing specific commissioning milestones, task durations, allocated resources and progress to date; and
- *daily commissioning schedules* as sub-sets of the three weekly schedule detailing tasks to be conducted over the next 24 h and allocated resources.

4.3. Roles and responsibilities in plant commissioning

Table 1 summarizes the roles and responsibilities for the owner (Newcrest), managing contractor (Bechtel Minproc Joint Venture) and contractors, for the commissioning of the Cadia Gold/Copper Project (Churchill and Lane, 1997). This structure is favoured for larger, more complex projects, in particular those containing EPC sub-contracts.

Smaller projects differ depending on contracting strategy. It is not abnormal for the structure to be simplified and for the construction manager to take responsibility for some aspects of pre-commissioning or even to manage all aspects of commissioning. Fig. 1 illustrates an example organizational structure for commissioning of a moderate-size gold project. The responsibility for pre-commissioning falls to construction contractors, under the direction of the construction manager and his superintendents. Responsibility for commissioning is then handed over to the commissioning manager who, assisted by his commissioning team, undertakes water and ore commissioning, followed by performance trials. Sometimes, the commissioning manager may contribute to pre-commissioning, by taking responsibility for quality control, while reporting to the construction manager.

Table 1
Summary of roles and responsibilities in project commissioning for the Cadia Gold/Copper Project (from Churchill and Lane, 1997)

			Pre-commissioning					
Phase	Construction		Pre-operations Testing	System Checks		Commissioning	Operation	
Milestone		Construction Completion			Mechanical Completion			Practical (or Final) Completion
Owner								
Operations team	Owner review and support		Participate where appropriate in pre-op testing under direct management and responsibility to managing contractor's commissioning manager			Manage routine maintenance of operating plant. Operate plant under management of commissioning manager. Participate in post commissioning systems checks.	Take up management of operating plant	
Development/ engineer	Owner representative				Receive mechanical completion of plant from managing contractor.	Care and Custody transferred by formal letter.		Accept practical completion of prime contract
Managing Contractor								
Commissioning	QA role – interface between owner and construction with regard to detail of hand over documentation, review operability of plant.	Receive construction complete facilities	Manage all pre-op testing, system checks and no-load trials. Plan, co-ordinate and supervise horizontal package testing. Co-ordinate and witness vertical package testing.		Hand over of appropriate pre-commissioning packages to owner.	Manage all operational aspects of plant ore and load commissioning. Co-ordinate with construction on punchlist issues. Co-ordinate with owner operations on plant performance targets	Assist owner operations team with plant operation in a technical capacity. Plan and manage performance trial.	Ensure all plant documentation required by the owner is complete.

Table 1 (*continued*)

Phase	Construction		Pre-commissioning			Commissioning	Operation	
			Pre-operations Testing	System Checks				
Milestone		Construction Completion			Mechanical Completion			Practical (or Final) Completion
Construction	Construction management	Hand over of plant packages to commissioning team. Ensure that all installation testing documentation is complete and suitable for handover.	Manage all aspects of plant rectification/ modification		Retain care and custody of plant. Organize and manage maintenance contractors for operating services and relevant plant	Manage mod squad		Outstanding issues punchlisted. Terminate mod squad on completion.
Engineering	Engineering support and drawing updates							
Contractors								
Vertical contracts	Construction	Review of installation testing documentation by construction and commissioning managers	Plan and supervise testing. Co-ordinate with managing contractor		Ensure all pre-commissioning documentation is complete and handover to commissioning manager. Transfer plant ownership, and care and custody to managing contractor	Co-ordinate with commissioning manager with respect to performance trials. Provide labour to construction manager as required.		Vertical package contact complete
Horizontal contracts	Construction	Review of installation testing documentation by construction and commissioning managers	Conduct pre-op testing under general supervision of commissioning manager	Participate in systems and no-load testing	Hand over all completed pre-op test data. Horizontal contract package complete. Punch list items identified. Effective practical completion	Provide labour to construction manager as required		

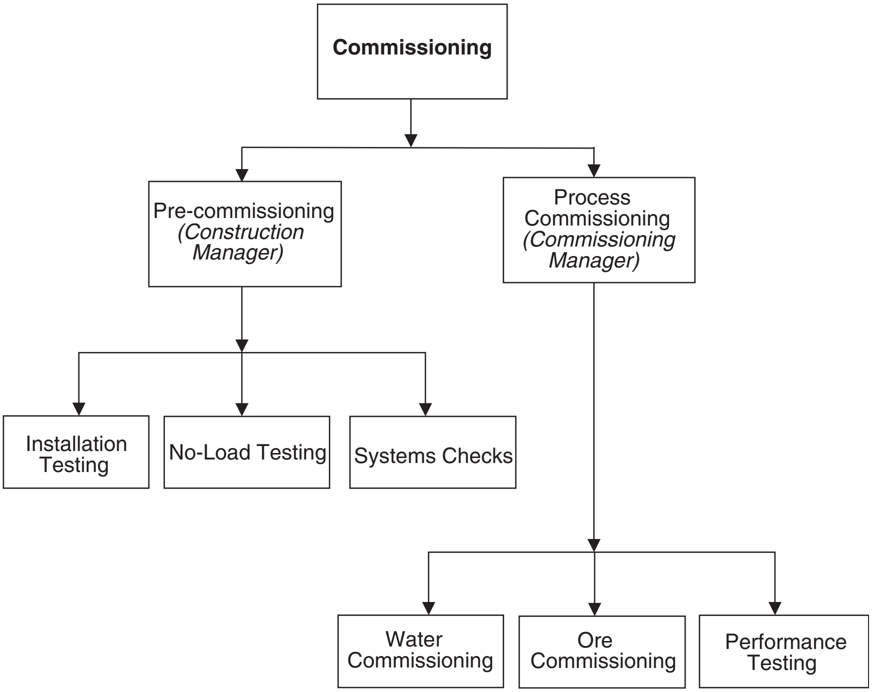

Fig. 1. Example of commissioning responsibilities for moderate-size gold plants.

The commissioning team may be responsible for the following tasks:

- preparation and updating the commissioning schedule, procedures and budgets;
- administration of safety clearances and tagging procedures for control purposes, for safety of commissioning personnel and for protection of plant equipment during commissioning;
- coordination of vendor representatives for commissioning;
- notification to the owner in writing of all intentions to test, typically via daily meetings;
- coordinating handover of commissioned plant areas in satisfactory condition to the owner, along with appropriate documentation. Records of pre-commissioning testing are forwarded to the Owner as part of the handover package; and
- coordinating with the construction manager on the finalization of punchlist tasks.

4.4. Packaging the commissioning process

Handover packages are compiled on completion of construction for turn over to the commissioning manager and on achieving mechanical completion or on achieving final completion, depending on the contract, for handover to the owner.

The handover package includes all testing documentation, equipment manuals, contract status statements, punchlists, as-built drawings and all other documentation pertinent to the facility, area or unit operation completed.

The packages detail the tests completed, the contractual status, as-built drawings, punchlists and all other information pertaining to the facility. Details of typical package content are provided by Churchill and Lane (1997).

The total plant is typically split into unit process based packages comprised of data for facilities, systems and sub systems. An example is provided in Fig. 2.

4.5. Input from vendors

Vendor representatives may have input and site representation during installation, installation testing, water commissioning, ore commissioning and performance testing. An important contractual role is confirmation that the installation is in accordance with requirements and that vendor warranties are in place.

The budgeting and control of vendor representatives is jointly managed by the construction and commissioning team. The total budget for vendor representatives on large projects can amount to millions of dollars. Participation on small projects may be restricted to final sign-off of installation or specialist set-up.

When several days of travel are required to and from a remote or overseas site, the costs for each vendor representative attending site increases significantly. A decision may be taken to have vendor representatives attend site for only key items of equipment. If this is the case, commissioning team manning levels need to account for the work otherwise conducted by vendor representatives.

The managing contractor's commissioning team should have sufficient experience to determine the requirement for vendor representation, and sufficient expertise to determine when vendor warranties should be exercised.

4.6. Safety considerations

The principal aim in all construction and commissioning is to ensure the safety of all participants while completing the necessary work. This is facilitated through the planning process and the rigorous application of an isolation and tag-out procedure for testing of all energized systems.

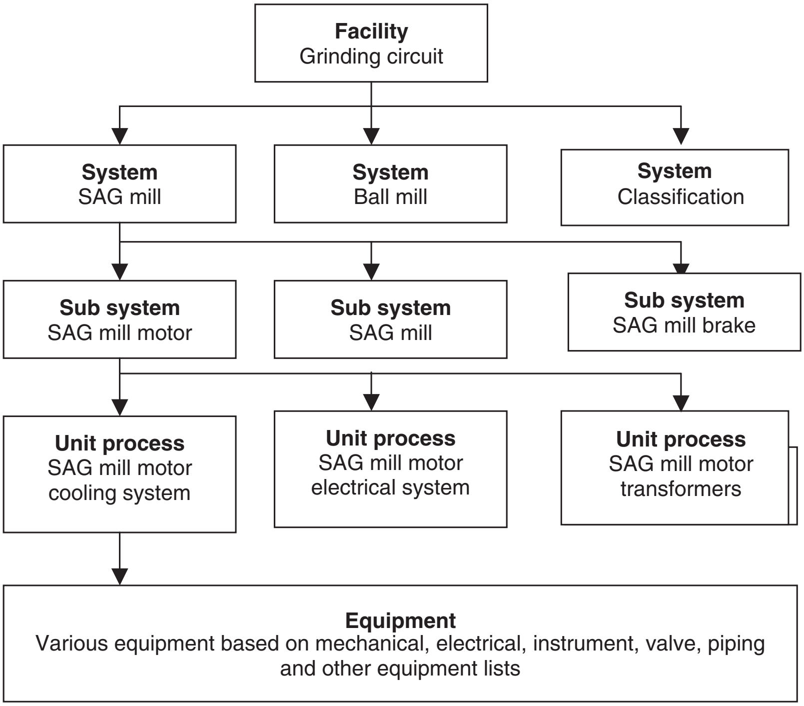

Fig. 2. Example of package-based commissioning structure (for large SAG mill motor unit processes).

The isolation and tag-out procedure is more rigorous in commissioning than later plant operation due to the concurrent construction, testing and operation of plant facilities and the lack of familiarity of construction workers with plant operation requirements, as well as plant operators with construction requirements. The procedure needs to clearly define the isolation of equipment for maintenance or modification and the associated tagging process. Particular care is needed on brownfields sites, where commissioning of new equipment occurs alongside an operating plant.

Cleanliness inspections are an important part of the pre-commissioning process and should be completed for all facilities prior to each of the various stages of testing.

5. PRE-COMMISSIONING

The definition of pre-commissioning may vary from project to project. For the purpose of this discussion, pre-commissioning will follow the example shown in Fig. 1 and comprise:

- Installation testing
- No-load testing and
- Systems checks.

Through these activities, individual items of equipment and installations are tested without introduction of water, ore, slurries or reagents.

Sufficient resources must be in place to do a thorough job of testing. Incomplete testing leaves doubts as to functionality, creates extreme credibility problems and must therefore be avoided.

5.1. Personnel

The number of personnel involved in commissioning is a function of the size and complexity of the project. For a typical gold project, with the responsibilities shown in Fig. 1, pre-commissioning will involve the following personnel:

- Owner's representative(s), for witnessing tests.
- Managing contractor's team:
  - ○ construction manager;
  - ○ commissioning manager (if required to assist with quality control);
  - ○ commissioning administrator (recommended to handle the piles of paperwork on all except smaller and less complex projects);
  - ○ construction superintendents:
    - – mechanical/piping;
    - – electrical/instrumentation;
- Vendor engineers and technicians
- Sub-contractor's commissioning team:
  - ○ supervisor; and
  - ○ tradesmen/commissioning technicians (to do the work).

The owner's operating and maintenance personnel can contribute to pre-commissioning. This can assist with seamless transfer of a facility from the contractor to the owner, as these personnel gain early experience of the plant. The effective use of the owner's team is dependent on the owner's ability to bring on personnel early and ensure that sufficient time is available for training and preparation.

5.2. Testing sequence

Project commissioning is ideally conducted in the following sequence:

1. Infrastructure used during construction, including warehouses, offices and laydown areas, and temporary services (sewerage, power and water).

2. HV switchyard.
3. Sub-stations and motor control centres (MCCs) (particularly those supplying water and air services).
4. Water supply, storage and distribution systems.
5. Water and air distribution services necessary to conduct pre-operational testing in the main plant.
6. External facilities required for plant operation, such as crushing plants and tailings dams.
7. Reagent and similar services in the main plant and
8. Main operating plant.

The aim of the above sequence is to ensure that all services are operable prior to completion of the main plant, allowing focus on the main plant in the period immediately prior to process commissioning.

5.3. Installation testing

Installation testing is the verification that the facility has been constructed in accordance with the relevant design documents and also verification of the operational acceptability of each item of equipment. Typically, it will include hydrostatic and pneumatic pressure tests, flushing of lines, lubrication, alignment checks, electrical point-to-point checks, megger tests and component identification checks, motor direction tests, all drives run, conveyors run and tracked, instruments checked, control system verified and facility sequence testing. All equipment and systems are cleaned out prior to water commissioning.

Construction personnel are generally responsible for installation testing. Handover from construction to commissioning is accompanied by a package indicating the general status of the works and associated contracts, as described previously.

5.4. No-load testing

No-load testing is the extended operation of equipment without ore or water to verify its readiness for process commissioning. This phase applies to equipment such as crushers, conveyors and agitators.

5.5. Systems checks

The checking of control systems is considered here part of pre-commissioning, as the objective is to verify that the installation is in accordance with the plant design and the activity requires completion prior to water commissioning.

6. PROCESS COMMISSIONING

6.1. Who commissions the plant?

The organizational structure for the management and control of the commissioning phase is dependent on the contract structure.

For LSTK projects, the managing contractor controls all aspects of plant commissioning through to final completion, although the owner exerts ultimate control, as the managing contractor aims to hand over the plant in the shortest time frame. Owner's personnel commonly operate and maintain the plant under the direction of the managing contractor's commissioning manager.

For EPC and EPCM contracts, the management and control of ore commissioning may fall to either the owner or the managing contractor. The owner may wish to control commissioning where the owner's team has extensive commissioning or operating experience with similar processing plants.

6.2. Personnel selection

The number of personnel involved in commissioning is a function of the size and complexity of the project. For a moderately large EPCM project the people required to complete pre-commissioning include:

- Owner's representative(s), for witnessing tests;
- Managing contractors team:
  - commissioning manager;
  - commissioning administrator (if required);
  - commissioning engineers:
    - process/metallurgical
    - electrical/instrumentation
    - mechanical/piping
    - DCS/control;
  - 'mod squad':
    - supervisors;
    - tradesmen
- Vendor engineers and technicians.

The task of leading a commissioning team requires that the commissioning manager has sufficient experience to command the respect of the construction, commissioning and owner's teams, and has the flexibility to adjust the approach to maximize outcomes at minimum cost outlay. The ability to manage the handover process and work with both the construction manager and owner's team is important.

The commissioning process commonly results in a requirement for modifications to piping, platework, instrumentation and electrical systems, as well as adjustments to mechanical equipment. Such work is preferably undertaken by a dedicated team, the 'mod squad', in order to divorce it from contract work and agreed variations. The 'mod squad' is commonly formed from members of the construction and installation contractors, as their contract work winds down, and reports to the commissioning manager.

While the responsibility for commissioning varies with the nature of the contract, the owner's operators and tradesmen usually operate and maintain the facility, following the introduction of ore, under the direction of the responsible party. In all cases, the operation of the plant should be conducted through the owner's management structure.

A balance between training and achievement is required to arrive at a successful commissioning outcome. Failure to communicate and train owner's staff will result in alienation and friction between commissioning personnel and operators. If the owner's personnel are unready when the plant is handed over, plant performance is likely to drop for a period following departure of the commissioning team. This will result in a greater loss to the project than the loss resulting from the extra time taken to effectively implement actions on a team basis.

There have been mixed experiences where owner's operational personnel have been co-opted into systems checks and water commissioning. Ill-prepared owner's operators can interpret a high frequency of installation 'faults' as poor-quality engineering and construction. This can lead to a loss of confidence in the plant on the part of the operators, which is detrimental to a successful handover.

6.3. Water commissioning

On completion of pre-commissioning of a plant area, the responsibility for commissioning generally passes to the commissioning manager. Water commissioning consists of successfully testing and operating items of equipment grouped together into modules. The modules will be operated as close as practically possible to normal plant operating conditions and upset conditions will be simulated.

Water commissioning activities typically include:

- filling tanks and vessels with water;
- pumping water along liquid and slurry lines;
- simulation of operating conditions, using water and air, where practical;
- testing of systems with operating equipment;
- ensuring plant operates in accordance with the control philosophy; and
- surveillance for abnormal conditions.

The use of system demonstrations at the conclusion of water commissioning is a positive approach. Operations personnel should be invited to test any and all process control interlocks and sequences with the support and advice of the commissioning team to assist them in understanding the total system.

6.4. Ore commissioning

The objective of the effort put into pre-commissioning and water commissioning is to provide a plant that is ready to operate. If this is the case, ore commissioning should not be a prolonged problem-solving session. Shutdown of the plant should be on a planned basis, and solely to check, adjust or modify equipment during the run-in phase and to conduct planned maintenance.

The commencement of ore commissioning exposes the project to increased risk. The potential for equipment to be maltreated or damaged is high and resultant delays will impact on project economics. The planning and scheduling of ore commissioning aims at minimizing risk.

The detailed planning and scheduling conducted for plant pre-commissioning should be carried through to plant ore commissioning. An effective planning process for ore commissioning includes the owner ensuring the supply of sufficient and suitable ore, consumables and maintenance spares, together with adequately trained personnel. The managing contractor should ensure that the owner is fully aware of the detailed requirements to avoid possible conflict and loss of production.

6.5. Operations and maintenance training

Plant operators should understand the basic conceptual process and its method of application, including the interactions between various plant modules (e.g., grinding and CIL or water balance/storage impacts on plant operation). Plant operators also require some exposure to the duties and practices required to operate the plant. Tradesmen should ideally become acquainted with the plant by becoming involved in pre-commissioning activities as previously discussed. This also ensures that any deficiencies in skills are identified prior to plant start-up, allowing for the implementation of appropriate training without impacting on plant operation.

Training packages may be prepared for operating and maintenance positions. These can include simulation packages so that personnel experience typical operating problems prior to plant operation.

Maintenance personnel should be fully acquainted with the maintenance requirements of any novel equipment, including selected visits to vendor shops for specialist training. Informal training sessions, as part of visits by vendor representatives, can introduce personnel to unfamiliar equipment.

6.6. What happens when things go wrong

At times, things go wrong during commissioning. Although it is often necessary to attack symptoms in the short term, it is important to analyse the problem and identify the root cause before attempting to prepare a plan to rectify the problem. The plan must be communicated to all stakeholders; otherwise, confidence in the commissioning process may be lost.

6.7. Principal causes of poor commissioning outcomes

The principal causes of poor ore commissioning outcomes are listed below:

- *poor process definition* resulting from lack of testwork, inadequate design data or poor process design;
- *incorrect equipment* specification, selection or vendor advice in design;
- *lack of experience* and expertise in design, construction or commissioning;
- *lack of planning* and scheduling of activities during construction and commissioning;
- *inadequate consumables and spares* supply resulting from lack of planning;
- unsatisfactory refurbishment of second-hand equipment;
- design, construction or installation errors in pipework, wiring and control logic;
- *inappropriate commissioning management* (too many chiefs and lack of communication); and
- *errors* in testing, operating and maintenance.

All issues should be discussed openly. Poor communication between parties can lead to poor contractual relations and will result in less than optimum commissioning outcomes. Even the most catastrophic design error is best identified prior to ore commissioning, thus allowing for the development of contingency plans to minimize the impact.

7. PERFORMANCE TESTING

Performance tests are often required of a contractor to demonstrate that a plant is *fit for purpose*. The performance tests are often comprised of throughput tests and process tests and require that both the owner and the contractor meet listed criteria.

7.1. Contractor warranties

Typically, the contractor warrants that the plant will achieve each of the following throughput tests:

- maximum primary crusher throughput over a 1-h period;
- average primary crusher throughput over a 7-day period with an 80% passing size of the crushed-ore product of the crushing circuit no larger than, for example, 150 mm; and
- grinding circuit throughput over a 7-day period with an 80% passing size of the grinding circuit product (cyclone overflow) no larger than, for example, 106 μ.

Typical process tests include the following:

- flotation recovery comparable to that obtained in laboratory locked cycle tests;
- soluble gold values in the CIL circuit tailings solution of, for example, less than 0.02 mg/L;
- required advancement of carbon batches through the adsorption tanks, acid wash, elution and return to the adsorption tanks via the reactivation kiln;
- gold concentration remaining on the stripped carbon, for example, 100 g/t or less;
- gold concentration remaining in the barren eluate shall be, for example, 10 mg/L or less.

Other contractor warranties that may be required by the owner include:

- the crushing and other plant shall achieve the above requirements with minimal spillage, without the use of standby pumps and other equipment and without undue vibrations, and
- specific tests required by the owner or financier.

7.2. Owner warranties

The owner is typically required to warrant ore supply and the characteristics of the ore, such as ore hardness, gold grade and other relevant factors that may impact on the contractor's ability to achieve their warranties in the performance tests.

7.3. Process test completion

The aim of both the owner and the contractor should be that plant performance during commissioning and early operation negates the requirement to formally undertake the performance tests, in part or full. The owner must pass control of the plant over to the contractor for the duration of the tests and incurs all costs for testwork. The contractor may wish to complete performance tests as early as possible to achieve performance bonuses.

8. POST-COMMISSIONING OPTIMIZATION

Optimization of the plant by the project owner continues after plant commissioning with the aim of maximizing plant throughput within the limitations of ore supply and the maximum capacity of the high capital cost unit processes. This is typically the comminution circuit or downstream concentrate treatment process (e.g., POX or bio-oxidation plant) for refractory gold ores. Recovery and operating costs are other targets for optimization.

The Macraes Gold Project treats sulfide ore, oxide ore (in campaigns) and retreats some tailings. The expansion in the throughput of the Macraes Gold Project since plant commissioning in 1990 is illustrated in Fig. 3. The periodic high treatment rates for oxide ore represent periods when the main grinding circuit was used to process oxide ore, during 1991, just prior to plant upgrade in 1999, and twice to process stockpiled oxide ore, in 2001 and 2003. The low rate of continuous treatment of oxide ore through a new mill can be seen post May 2003.

The following step changes occurred in plant throughput as a result of plant debottle-necking and mine expansion:

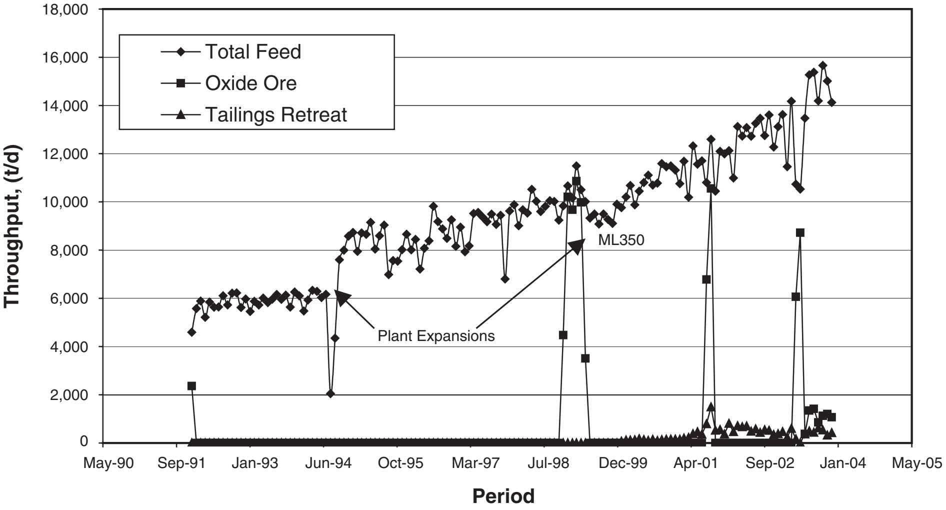

Fig. 3. Macraes Gold Project plant feed rate trends.

1. In late 1994, the plant was expanded by the addition of flotation and fine grinding capacity. The primary grind size was increased and ultra-fine grinding of flotation concentrate installed to improve gold recovery from flotation concentrate in the subsequent CIL circuit.
2. In late 1999, a further expansion of the plant was undertaken with the addition of a ball mill (ML350) to reduce the primary grind size and allow a further increase in throughput. In addition, a POX plant was installed to improve refractory gold recovery through oxidation of the flotation concentrate.
3. In late 2001, a retreatment flotation circuit was installed to recover gold from old sulfide tailings and in mid-2003, a further single-stage SAG mill was installed to allow for the parallel treatment of oxide ore or additional sulfide ore.

Each plant expansion was followed by a steady increase in plant throughput. The only element of the plant that had become redundant at the time of publication was the ultra-fine regrind facility that was shut down in 1995 due to higher-than-expected operating costs.

9. DEFINITIONS

Terms and their definitions vary from project to project. The following definitions apply to the terms used in much of this section as well as Fig. 1:

Commissioning. It encompasses all activities required to bring the plant from the construction phase to operation on ore and reagents.

Pre-commissioning. It is a subset of commissioning and comprises three activities, namely, installation testing, no-load testing and systems checks. The construction manager is commonly responsible for pre-commissioning.

Process commissioning. It is also a subset of commissioning and consists of water commissioning, process commissioning and performance testing. The commissioning manager is responsible for process commissioning.

Installation testing. It is part of pre-commissioning and is the verification that the facility has been constructed in accordance with the relevant design documents and verification of the operational acceptability of each item of equipment.

No-load testing. Pre-commissioning includes *no-load testing*, which is the extended operation of equipment without ore or water to verify its readiness for process commissioning.

Systems checks. They are considered a part of pre-commissioning and verify that the installation is in accordance with the plant design. This activity requires to be completed prior to water commissioning.

Water commissioning. It is testing and operating of groups of equipment using water in the absence of ore or reagents and is part of the process commissioning process. Preliminary tuning of controllers is conducted and logic is checked to verify readiness to receive ore.

Ore commissioning. It includes all activities conducted after mechanical completion and following introduction of ore and reagents.

Managing contractor. The *managing contractor* is the party responsible for providing project management. In some cases this may be the owner's engineer.

Owner's engineer. The *owner's engineer* is the representative of the owner for the purposes of the project. Where not otherwise specified, owner also refers to the owner's engineer.

Construction manager. The *construction manager* is the managing contractor's authorized representative managing the construction phase.

Commissioning manager. The *commissioning manager* is the managing contractor's authorized representative managing the commissioning phase.

Mechanical completion. It is reached when all pre-commissioning and water commissioning is complete and the facility is considered ready to receive ore. All appropriate documentation has been submitted to the owner for the applicable section of plant. All valves, switches, circuit breakers and operational equipment in the identified area should be clearly and appropriately tagged and documented.

The term *practical completion* is commonly used for this stage of commissioning, but has been avoided in this section owing to the many different definitions of this term.

Final completion. It signifies satisfactory completion of plant performance tests and all other contractual requirements.

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I.3 *Safety, Process Control and Environmental Management*

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Chapter 8

International cyanide management code

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Since the early twentieth century, simple cyanide salts or solutions have become clearly the dominant reagent used by the mining industry for the extraction of gold from ore. While cyanide is a chemical with significant associated hazards, the simple fact is that no commercially viable and environmentally sound alternative lixiviant currently exists, despite significant research efforts in this regard (McNulty, 2001).

The development of an International Cyanide Management Code (*the Code*) is seen as an important and responsible action by gold producers, cyanide manufacturers and associated transportation companies to augment existing regulatory requirements or fill in gaps when such regulatory requirements are lacking. The Code provides comprehensive guidance for best practice in the use and management of cyanide at gold mines around the world and reaches beyond the requirements of most governments and regulatory agencies. A significant body of technical and administrative work in developing the Code has already been carried out by a large and varied international group of contributors and stakeholders. The challenge now exists to carry this forward to practical implementation and administration.

1. BACKGROUND TO THE CODE

The world's attention became focused on the use of cyanide within the gold industry in January 2000, following the accidental release of cyanide-bearing tailing solution from the Aurul mining operation near Baia Mare, Romania. The spill led to approximately 100,000 m^3 of solution entering initially the Sasar River, before eventually depositing into the Danube River via a series

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of tributaries. It is estimated that between 50 and 100 t of cyanide (as CN) was released into the river environment (Schlingemann *et al.*, 2000).

The incident sparked an immediate impact assessment mission, coordinated jointly by the United Nations Environment Programme (UNEP) and the United Nations Office for the Coordination of Humanitarian Affairs (Schlingemann *et al.,* 2000). This was followed up by an International Task Force Investigation, initiated by the European Union (EU) Commissioner for the Environment (Garvey *et al.*, 2000). In conjunction with the investigation, UNEP and the International Council on Metals and the Environment (ICME) convened a multiple-stakeholder workshop in May 2000. The key outcome was the establishment of a framework for an international code of practice for the use of cyanide in the gold-mining industry, and the establishment of a Steering Committee to coordinate code development (Balkau and Nash, 2000). While the code has been referred to under several equivalent titles, the accepted nomenclature is the International Cyanide Management Code for the gold-mining industry.

The participation and contribution of a diverse range of stakeholders was important to the success of the initial workshop. Forty delegates were involved, representing such organizations as the United Nations, the EU, the World Bank, the OECD, the ICME, various governments, environmental advocacy groups, gold mining companies and industry associations, the Gold Institute, and various expert technical consultants. This methodology was continued in the makeup of the Steering Committee and subsequent development of the Code.

2. CODE DEVELOPMENT AND ADMINISTRATION

The multiple-stakeholder Steering Committee first met in December 2000, and guided Code development for a period of 14 months following inception. The development stage included extensive consultation with stakeholders and organizations globally. The project culminated in the issuing of a press release in March 2002, summarizing work to date and announcing the Code's imminent completion, with the publishing of final Code documents occurring in May 2002 (Fig. 1).

The Code was viewed as unique in two aspects. It was the first voluntary industry Code of Practice requiring its signatories to demonstrate compliance through independent third-party professional audits, and it represented the first time that such a broad-ranging international multi-stakeholder group had worked cooperatively to produce a global voluntary program for specific industry improvement.

The unique nature of the Code resulted in difficulty finding an existing organization that was prepared to house the Code, and the issue was further

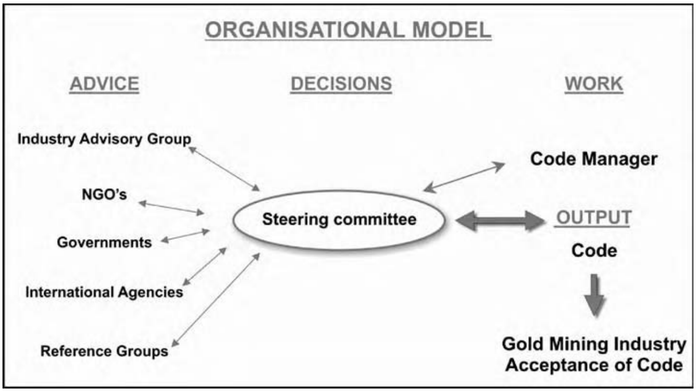

Fig. 1. Cyanide Code Organisational Model.

complicated by the need for the organization to have an independent, multi-stakeholder overview.

To meet this challenge, the decision ultimately was made, after determining that no existing organization provided the correct forum, to create a new institute known as the International Cyanide Management Institute (ICMI). The ICMI was officially incorporated (CA, USA) as a non-profit corporation in October 2002, and was charged with the responsibility of administering the Code through a multi-stakeholder Board of Directors consisting of representatives of the gold-mining industry and participants from other stakeholder groups.

The ICMI made progress on many fronts. However, Code rollout was hampered by several factors, including unfinished administrative procedures for Code management, a lack of funding, and the dissolution of the Gold Institute, which had hitherto provided a coordinated industry input via its Industry Advisory Group (IAG). In this interim period, many gold producers took the opportunity to conduct gap analysis to determine deficiencies with the Code, implement corrective actions to resolve identified deficiencies, and complete internal self-audits to assess implementation of feasibility and cost, a not inconsiderable task.

In February 2004, the IAG was reconstituted by a group of gold producers, with the aim of providing industry coordination to facilitate Code implementation. Members of the reconstituted IAG, which included leading gold producers and cyanide manufacturers, released a public joint statement of support for the Code in June 2004. At the time of writing, the IAG was in earnest correspondence with the ICMI to formulate a strategy to finalize Code implementation.

A key challenge that has always faced the gold industry is to encourage take-up of the Code by small gold producers. While most of the larger gold producers have been involved in the Code from its inception, the Steering

Committee and the IAG have recognized the importance of promoting the virtues of the Code to small producers.

3. CODE CONTENT

The intent of the Code is articulated in its Mission Statement, which reads:

> *To assist the global gold mining industry in improving cyanide management, thereby minimizing risks to workers, communities and the environment from the use of cyanide in gold mining, and reducing community concerns about its use.*

The objectives of the Code as identified by the Committee are:

- *To protect workers, communities and the environment from adverse effects of cyanide.*
- *To improve cyanide management.*
- *To be used by large and small gold mining companies, cyanide manufacturers and transporters.*
- *To serve as a form of assurance for interested parties including regulators, financiers, communities and non-governmental organizations.*
- *To be applied internationally, in both developed and developing countries.*
- *To be credible and verifiable.*
- *To be dynamic over time.*

The Code consists of nine principles, within each exist several Standards of Practice. The Principles broadly state commitments that signatories make to manage cyanide in a responsible manner. The Standards of Practice are essentially the *nuts and bolts* of the Code, and identify performance goals and objectives that must be met to comply with the principle.

The nine principles are summarized in Table 1.

The thirty-one Standards of Practice are summarized in Table 2.

4. CASE STUDY – OPERATING SITE COMPLIANCE STRATEGY

Consistent with modern mine management, self-assessment is an important tool in meeting Code requirements. Sites will generally conduct an initial internal assessment, the practical outcome being an action plan to address items of significance. This may then be followed by assessment by an external audit team, often coordinated by corporate technical staff. This assessment is very important, as it allows site personnel to experience the audit process prior to an official Code audit. The following section gives insight into this sequence of events at AngloGold Ashanti's Sunrise Dam Gold Mine (SDGM).

Table 1
Summary of code principles

Principle no.	Discipline	Intent
1	Production	Encourage responsible manufacturing by only using cyanide produced in a safe and environmentally protective manner
2	Transportation	Protect communities and the environment during cyanide transport
3	Handling & storage	Protect workers and the environment during cyanide handling and storage
4	Operations	Manage cyanide process solutions and waste streams to protect human health and the environment
5	Decommissioning	Protect communities and the environment from cyanide through development and implementation of decommissioning plans for cyanide facilities
6	Worker safety	Protect worker health and safety from exposure to cyanide
7	Emergency response	Protect communities and the environment through the development of emergency response strategies and capabilities
8	Training	Train workers and emergency response personnel to manage cyanide in a safe and environmentally protective manner
9	Dialogue	Engage in public consultation and disclosure

The SDGM, 100% owned by AngloGold Ashanti Limited, lies within the Mt. Margaret Mineral Field in the Shire of Laverton, Western Australia. The mine is located approximately 730 km northeast of Perth, and some 55 km south of the town of Laverton. SDGM commenced operation in 1997, and in July 2004 poured its two millionth ounce of gold.

SDGM was initially developed as a 1 Mtpa oxide-treatment plant utilizing conventional crushing, ball milling and carbon-in-leach (CIL) processing. Subsequent upgrades in 1999 and 2000, combined with continuing optimization and de-bottlenecking, has resulted in the current treatment rate of 3.5 Mtpa.

Cyanide is utilized on site in three sections of the process facility. It is used within the CIL circuit as the primary gold lixiviant. It is also used as a lixiviant within the gravity gold recovery circuit, leaching gravity concentrates within the Acacia fluidized-bed leach-reactor. The final use for cyanide is within the elution circuit, where it is used to desorb gold from activated carbon.

Prior to the creation of the Code, AngloGold Ashanti employed internal control measures to ensure adequate cyanide management premised on

Table 2
Summary of Code Standards of Practice

Standard of practice	Principle	Summary of intent
1.1	Production	Purchase cyanide only from manufacturers that employ practices and procedures to limit exposure of their workforce to cyanide and to prevent releases of cyanide to the environment
2.1	Transportation	Establish clear lines of responsibility through written agreements between producers, distributors and transporters for safety, security, release prevention, training, and emergency response
2.2	Transportation	Require that cyanide transporters implement appropriate emergency response plans and capabilities and employ adequate measures for cyanide management
3.1	Handling & storage	Design and construct unloading, storage and mixing facilities consistent with sound and accepted engineering practice and employing quality control/quality assurance procedures and spill prevention and containment measures
3.2	Handling & storage	Operate unloading, storage and mixing facilities using practices and procedures including inspections, preventive maintenance, and contingency plans to prevent or contain releases and control and respond to worker exposures
4.1	Operations	Implement management and operating systems, practices and procedure including contingency planning and inspection, and preventive maintenance procedure designed to protect human health and the environment
4.2	Operations	Introduce management and operating systems to minimize cyanide use and thereby limit concentrations of cyanide in mill tailings
4.3	Operations	Implement a detailed and comprehensive water management program to prevent unintentional releases, such as maintaining adequate freeboard in tailings storage facilities
4.4	Operations	Implement measures to protect birds, other wildlife, and livestock from adverse effects of cyanide-process solutions
4.5	Operations	Implement measures to protect fish wildlife from the direct and indirect discharges to surface water
4.6	Operations	Implement measures designed to manage seepage from cyanide facilities to protect the beneficial uses of groundwater

Table 2 (*continued*)

Standard of practice	Principle	Summary of intent
4.7	Operations	Provide spill prevention or containment measures for process tanks and pipelines
4.8	Operations	Implement quality control/quality assurance procedures to confirm that cyanide facilities are constructed according to accepted engineering standards and specifications
4.9	Operations	Implement monitoring programs to evaluate the effects of cyanide use on wildlife and surface and groundwater quality
5.1	Decommissioning	Plan and implement procedures for effective decommissioning of cyanide facilities that are protective of human health, wildlife, and livestock
5.2	Decommissioning	Establish an assurance mechanism capable of fully funding cyanide-related decommissioning activities
6.1	Worker safety	Identify potential exposure scenarios and take measures as necessary to eliminate, reduce, or control them
6.2	Worker safety	Operate and monitor cyanide facilities to protect worker health and safety and periodically evaluate the effectiveness of health and safety measures
6.3	Worker safety	Develop and implement emergency response plans and procedures to respond to worker exposure to cyanide
7.1	Emergency response	Prepare detailed emergency-response plans for potential cyanide releases
7.2	Emergency response	Involve site personnel and stakeholders in the planning process
7.3	Emergency response	Designate appropriate personnel and commit necessary equipment and resources for emergency response
7.4	Emergency response	Develop procedures for internal and external-emergency notification and reporting
7.5	Emergency response	Incorporate remediation measures that account for the additional hazards of using cyanide treatment chemicals, and monitoring elements in response plans
7.6	Emergency response	Periodically evaluate response procedures and capabilities and revise them as needed
8.1	Training	Train workers to understand the hazards associate with cyanide use
8.2	Training	Train appropriate personnel to operate the facility according to systems and procedures that protect

Table 2 (*continued*)

Standard of practice	Principle	Summary of intent
		human health, the community, and the environment
8.3	Training	Train appropriate workers and personnel to respond to worker exposures and environmental releases of cyanide
9.1	Dialogue	Provide stakeholders the opportunity to communicate issues of concern
9.2	Dialogue	Initiate dialogue describing cyanide management procedures and responsibly address identified concerns
9.3	Dialogue	Make appropriate operational and environmental information available to stakeholders

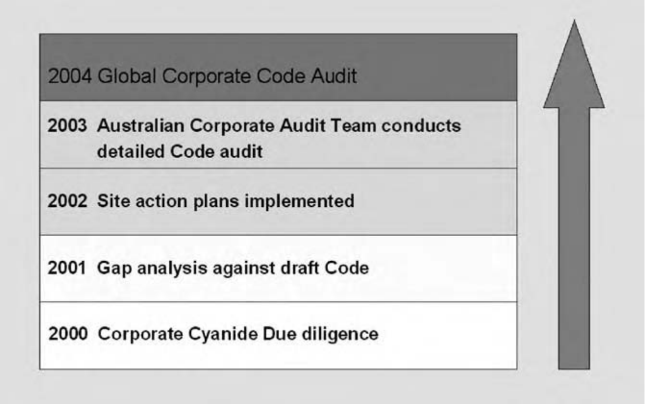

Fig. 2. Recent evolution of cyanide management at Sunrise Dam Gold Mine.

industry best management practices. The Code was integrated into this system over a period of time, and has now become the primary means of measurement and systems control.

The timeline of development for SDGM is shown in Fig. 2.

Prior to the availability of the Code as a reference document, internal AngloGold Ashanti standards were utilized to assess site practices and procedures (Lethlean, 2002). When early drafts of the Code became available in 2001, a Gap analysis was carried out against the Code verification protocols. Integral to the effectiveness of this analysis was the direct involvement of site personnel.

As a practical adjunct to the Gap analysis, site management undertook a series of Hazard and Operability studies (HAZOPs) to better evaluate site practices and procedures against Code criteria. The studies were divided into three plant sections – General Processing Plant, Cyanide Storage Facility, and Gold Room. The HAZOPs were undertaken utilizing an external facilitator and personnel from all sections of the processing team, including metallurgists, process technicians, safety personnel, electrical and maintenance personnel. The cyanide supplier (AGR) also participated and provided valuable input.

The Gap analysis revealed that overall site management and use of cyanide was good; however, some areas for improvement also were identified. A detailed action plan was compiled from the Gap analysis, with key elements for attention being grouped in Engineering and Procedural categories (Noble, 2003). A selection of key elements is summarized.

Engineering:

- Colour coding and labelling of all cyanide related pipelines, tanks and valves.
- Provision of secondary containment for cyanide pipelines.
- Installation of leak detection flange covers in the elution circuit.
- Installation of static HCN gas detectors in appropriate plant sections.
- Installation of hard-wired magnetic flowmeters to appropriate slurry and solution pipelines.
- Process-control modifications.
- Modifications to existing sumps.

Procedural:

- A review of the sodium cyanide supply contract to ensure that the supplier is a member of an appropriate Chemical Association Responsible Care program.
- Modification to sodium cyanide supply contract to ensure provision of appropriate supporting documentation.
- The extension of existing site hazardous chemical training to include more comprehensive cyanide-specific content.
- Instigation of regular cyanide-related mock emergency drills, with review meetings and appropriate follow-up.
- Extension of existing water-sampling procedures to include more comprehensive cyanide analysis.
- Updating standard operating procedures.
- Amendment of the existing decommissioning and closure plan to clarify cyanide-related actions.
- Updating processing plant preventative maintenance in relation to cyanide-associated equipment.

- Written descriptions of cyanide-related management systems.
- Modification to the site Emergency Management Plan to include more specific information and instructions relating to cyanide.

A specific requirement of the Code that required significant analysis and attention is the provision of adequate worker protection from hydrogen cyanide gas (HCN). The Code stipulates a ceiling level of 4.7 ppm HCN. This issue caused much debate during Code development, due to conflicting standards and a belief by many parties that a 10 ppm ceiling level had been demonstrated as appropriate.

The challenge faced within the Sunrise Dam circuit, and applicable to many operations in the Western Australian Goldfields region, is the high salinity of process water. It is common for process facilities in this region to operate with process water of salinity greater than 100,000 mg/L total dissolved solids (TDS). The typical salinity of Sunrise Dam process water is 230,000 ppm TDS. For reference, seawater has a typical salinity of 30,000 ppm TDS.

The most common method of minimizing evolution of HCN gas from a given process slurry or solution is by elevating the pH via addition of an alkali such as lime. However, high-salinity levels complicate this process, owing to the buffering effect of dissolved cations such as magnesium, which inhibits the elevation of pH.

Several options were evaluated to address this issue, including alternative water supplies, installation of enclosed tanks, and the use of gas-scrubbing systems. However, it was concluded that the optimum solution was an integrated system that incorporated pH and cyanide measurement and online control, modified alkali dosing, online HCN-gas measurement, personnel access control, and upgraded personal protection equipment.

Key elements that were implemented included:

- The use of an automatic pH measurement and lime-dosing system to maintain the maximum practical pH levels.
- The use of an automatic sample filtration and potentiometric cyanide titrator to automatically control cyanide addition to the CIL circuit. This minimizes both the amount of cyanide present in the process slurry and also the time that personnel are required to spend on the CIL circuit.
- Increased automation of other process tasks to further minimize the operator time spent in potential HCN areas.
- Installation of static HCN gas analysers at locations of potential HCN evolution. The instruments are linked to the plant process-control system, and an alarm system activates if an HCN gas measurement of 4.7 ppm or greater is detected.

- In addition to an audible and control-room alarm, local flashing light indicators are activated to ensure that personnel do not enter the area, and any personnel already in the area immediately evacuate.
- Installation of flashing-light indicators that activate during the acid-rinse cycle of the elution, thus indicating to personnel that elevated levels of HCN may be present, and not to enter the area.
- A requirement for personnel entering potential HCN areas to check in with the mill control-room prior to entry.
- A requirement for personnel entering potential HCN areas to carry calibrated personal HCN monitors with alarm settings corresponding to Code requirements.
- A requirement for personnel entering potential HCN areas to carry a Durum HCN escape mask.

The obvious result of these various activities is consistency with the Code's Mission Statement of "minimizing risks to workers, communities and the environment from the use of cyanide." It was demonstrated that these modifications and controls, when audited against the Code criteria and Implementation Guidance document, resulted in full compliance; examples are given in Figs. 3–8.

The next stage in the evolution of site cyanide management was the completion of an "external" Code audit in December 2003. A three-person team from AngloGold Ashanti's Perth office conducted the audit. The chosen team had relevant experience in the areas of metallurgy, chemistry, engineering, safety, occupational health, environment and community matters, and hence was able to effectively cover all aspects of the Code criteria. An audit report and recommendations were issued to site management for action.

Fig. 3. Access control and warning system at entry to SDGM CIL section.

Fig. 4. On-line HCN gas analyser at SDGM CIL section.

Fig. 5. Automated cyanide titrator.

Due to the time and effort invested by the site team over the previous 3 years, the audit rating was favorable. However, there still remained issues requiring attention. One of the Code's key objectives is to remain dynamic over time, and it is important that a site-management plan also remains dynamic to avoid complacency.

Examples of items that are currently *work-in-progress* are:

- Minor technical amendments to the cyanide supply contract.
- Introduction of routine preliminary testwork to establish short-term cyanide demand from ore sources.

Fig. 6. Cyanide pipe colour coding and flange guards.

Fig. 7. Liquid cyanide storage tank and bund.

Fig. 8. Secondary containment for pipelines.

- Integration of existing but separate water-balance information systems into a single site-wide system.
- Review of selected secondary containment areas to assess permeability.
- Installation of a lime-slaking system and a modified dosing strategy to optimize pH control.
- Modification of the Emergency Response Plan to include cyanide-specific content and training.
- Development of additional opportunities for public comment and stakeholder liaison.

The next stage of assessment and ongoing improvement occurs soon after the time of writing, with a Corporate Cyanide Code Audit. In much the same way as the Australian (Regional) Corporate Audit, AngloGold Ashanti has developed an International Audit program to assess operating sites in all regions.

5. VERIFICATION AND CERTIFICATION

The Code documentation sets out the means and maintenance of certification. The audits are to be conducted every 3 years by independent, third-party professionals who meet the pre-defined criteria for auditors. Auditors evaluate an operation to determine if site management of cyanide is consistent with the Code's Principles and Standards of Practice. The Code's Verification Protocol contains the criteria for all audits.

During the initial verification audit, an operation's compliance at the time of the audit will be evaluated. This will provide baseline information, and forms the primary reference source for subsequent re-verification audits. Upon completion of the audit, the auditor must review the findings with the operation to ensure that the audit is factually accurate and make any necessary changes.

The Verification Protocol requires the auditor to make a finding regarding whether the operation is in full compliance, substantial compliance or is not in compliance with each of the Standards of Practice. Being in full compliance does not necessarily require an affirmative answer to all individual questions under a Standard of Practice. An operation may have used alternative means to meet the Standard or the Standard or one of its individual questions may have not been applicable for site-specific reasons.

The auditor must find that an operation is in compliance with the Code if the operation is in full compliance with all Principles and Standards of Practice. If not fully compliant, the auditor must identify where he or she believes that compliance has not been fully achieved and where improvements are necessary.

In order for the auditor to find that the operation is in substantial compliance with a Standard, the operation must have made a good-faith effort to comply and any identified deficiencies must be readily correctable and must not present an immediate or substantial risk to health, safety or the environment. Operations that are in substantial compliance with a Standard of Practice must develop an Action Plan to correct the deficiency. They must further commit to fully implement the Action Plan within a time period mutually agreed to with the auditor, but in no case longer than 1 year in order to be certified as in full compliance with the Code.

An auditor must find that an operation is not in compliance with the Code if it is neither in compliance nor substantial compliance with any one of the Standards of Practice.

An operation that is not yet active, but that is sufficiently advanced in its planning and design phases, can request conditional certification based on an auditor's review of its site plans and proposed operating procedures. An on-site audit is required within 1 year of the operation's first production of gold by cyanidation to confirm that the operation has been constructed and is being operated in compliance with the Code.

An operation or an individual cyanide facility at an operation is no longer subject to certification after decommissioning of the cyanide facilities.

The three possible certification outcomes for an operating site following an audit are outlined in Table 3.

In order to maintain certification, an operation must meet all of the following conditions:

1. The auditor has concluded that it is either in full compliance or substantial compliance with the Code.
2. An operation in substantial compliance has submitted an Action Plan to correct its deficiencies and has demonstrated that it has fully implemented the Action Plan within the agreed time.
3. There is no verified evidence that the operation is not in compliance with the Code.
4. An operation has had a verification audit within 3 years.
5. An operation has had a verification audit within 2 years of a change in ownership, defined as a change of the controlling interest of the operating company.

6. PRACTICAL ADVICE FOR AUDIT TEAMS

The author's experience in coordinating Code audits suggests that a three-person team is effective. The multi-disciplinary nature of the Code should be

Table 3
Code Certification Audit outcomes

Audit finding	Criteria	Outcome and further actions
Certified	Full compliance with all Principles and Standards of Practice	• Written compliance certificate • Status posted on Code website • Ongoing re-verification audits at 3-year frequency as defined by Code
Conditional certification	Full or substantial compliance with all Principles and Standards of Practice	• Written conditional compliance certificate • Status posted on Code website • Development of corrective Action Plan • Implementation of Action Plan within one year • Submission of documented proof of completion of Action Plan • Auditor verification if required
Uncertified	Any Principle or Standard of Practice assessed as less than substantially compliant	• Site must bring management programs and procedures into compliance with the Code • Arrange another Compliance Audit

reflected in the Audit Team make-up. Key disciplines that should be considered include Occupational Heath, Safety, Environment, Metallurgy, Engineering, and Community Relations. The Team should have a nominated leader to coordinate activities, and it is recommended that verification tasks be assigned to individual team members according to their areas of expertise.

A site audit can generally be completed in a 3-day period. To maximize the effectiveness of the audit, it should be considered for the team to remain on site for a further 2-day period to complete and issue a draft of audit report, and also to summarize the findings of the audit to site personnel.

Within a reasonable period prior to the audit commencing, the Audit Team should forward to site management an information package containing the audit protocol, anticipated requirement of site personnel, and a list of required documents for review (Audit Document Manifest).

The use of digital photography within the audit report is strongly advised, as it serves to confirm compliance issues, and allows illustration of specific findings and recommendations from the team.

It is recommended that the Audit Team become familiar with local statutory requirements relating to cyanide management that may apply to the operating site, as experience has shown that such requirements will usually form an integral part of site management procedures. Complementary to the

Code, they provide excellent guidance to the audit team on local regulatory conditions and their specific relation to Code requirements.

The collection of data verifying compliance is time-consuming, and experience has shown that it is very important to cross-reference supporting documentation during the audit process.

Some Standards of Practice within the Code contain many separate elements. For the Audit Team to form a judgement on the overall level of compliance within such Standards of Practice, it is necessary to develop scoring criteria.

7. PRACTICAL ADVICE FOR OPERATING SITES PREPARING FOR AUDITS

An audit is sometimes perceived as an unwelcome distraction by site personnel, particularly given their often heavy workloads and time pressure. However, for a given site scenario, an ill-prepared site team will invariably return a lower audit rating than one that has spent a little time preparing.

It is recommended that an operating site maintain a document reference system pertaining to the Code. This can be in electronic form, or as hard copies, preferably both. Such a system will greatly assist an Audit Team in the verification process, and also allow site personnel to keep track of modifications and updates to their operating plant and systems that are relevant to the Code.

A short pre-audit preparation meeting is recommended to allow better coordination of audit activities and arrangement of facilities. This will ensure availability of key personnel for discussions with the Audit Team during the visit.

The provision of a temporary data room for the Audit Team is very useful to consolidate verification documents. It is also recommended that as much documentation as possible is copied onto electronic media (*e.g.*, compact disc) for the use of the Audit Team. General sources of information on cyanide are also available digitally (Mudder *et al.*, 1998; Needham, 2003).

Finally, it is strongly recommended that site personnel carefully review the audit protocol requirements and questions, and ensure that all possible validation data is made available. In the author's experience, actual compliance ratings by an Audit Team are generally higher than perceived by site personnel. This is primarily due to lack of understanding of the audit criteria, and hence not making available all possible verification data.

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Chapter 9

Process control

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Gold plants are often operated with process control and optimization strategies that are inadequate and poorly supported. In recent times, however, plants are increasingly gaining substantial benefits by the installation and operation of good control systems that increase recovery, save costs and streamline operation. Typical benefits could be regarded as one or more of the following:

- a 15% reduction in the gold reporting to tailings;
- a 10% reduction in mill power;
- a 20% reduction in reagent consumption;
- a 10% increase in plant throughput;
- very few spillages and unscheduled shutdowns; and
- improved productivity and working conditions for plant personnel.

A large portion of the benefits obtainable from process control can be obtained from good basic control. Most of the infrastructure required for basic process control is standard and readily available commercially. However, people skilled in process control are usually in short supply, and they are attracted to jobs where advanced control is implemented. As a result, process control is often done well only when a special management or technical initiative for implementing good control is underway.

Process control should fulfil several direct technical aims. Intrinsically unstable process variables like sump levels and thickener underflow densities need to be stabilized and regulated at setpoints. Compensation might be

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required for measured disturbances, such as varying feeds to flotation plants. Quality-indicating measurements of final or intermediate products, such as particle size after milling, should be controlled when possible. Operating conditions should be regulated at optimum conditions, which themselves often need to be determined in a slower-acting strategy.

In the sections below, some important aspects are discussed in relation to the application of process control on gold plants. The 'weakest link' of these contributory aspects can constrain the degree of success possible.

1. MEASUREMENTS

Online measurements are key to a process control system. They warn the system of coming input disturbances and they provide feedback on variables that should be stabilized, regulated and optimized. Some of the most important variables measured on gold plants are as follows.

1.1. Solids flow on a conveyor belt

Nuclear meters and weightometers are standard and in common use for measuring solids flows on conveyor belts. Weightometers are often more accurate and give less 'noisy' signals. Nuclear meters are non-mechanical and can be more reliable and less costly. The calibration of these meters is typically done or checked by *belt cuts*, in conjunction with measurements of belt speeds. The positioning of the meters on conveyor belts is important, because the delay while the solids are on the belt can have an adverse impact on process control. The dynamics of feed belts can result in poor controllability of the solids feed, and the need for advanced control methods for good control.

1.2. Water flowrate

Magnetic-induction flow meters are the most common and reliable means of measuring the flow of plant water. Most of the meters are suitable only for cleaner waters, because of the problems of scale build-ups.

1.3. Slurry flowrate

Magnetic-induction flow meters are the most common and reliable means of measuring the flow of slurries. Calibration of these meters is often done by the physical measurement of water flows where this is possible. Sometimes this calibration is done off-site. If just trends of flow and not absolute values are important, measurements of pressure – *e.g.* at the feed to a hydrocyclone – can sometimes be used as a less costly substitute for a magnetic-induction flow meter. Pressure and flow usually correlate very well.

1.4. Density of slurry in a pipe

Slurry density is generally measured by a nuclear meter. It is important for it to be installed on a vertical pipe, and that the normal slurry flow through the pipe should be above 2 m/s, to minimize the adverse effects of settling. For the purposes of calibrating the meter, the pipe should conveniently be able to be filled with bubble-free water (*e.g.* there should be an isolating valve somewhere below the meter). A calibration can be done by (i) noting the meter reading with water in the pipe; (ii) obtaining the same reading with air in the pipe and inserting lead plates of appropriate thickness in the radiation path; and (iii) noting the reading (corresponding to a density of 2,000 $\mathrm{kg/m^3}$) with the lead plates still in place and water in the pipe too.

1.5. Mill power

Mill power is a good indication of the rate of grinding in a mill. Measurements of mill power generally contain unusually large components of noise. Their use is therefore often unnecessarily constrained to quite long-term control strategies. Actually, advanced electrical and digital processing of the signals from mill power meters can eliminate unwanted noise, leaving a fast-responding signal with good process information for control.

1.6. Slurry levels

Where there is little or no froth present, direct ultrasonic meters are often used reliably for level measurements. Problems can arise beyond extremes of measurement ranges if the meter gives unexpected outputs. Ultrasonic meters are also used quite commonly for flotation cells, but with floats and connected platforms located above the froth to reflect the ultrasound.

1.7. Angle of hydrocyclone underflow spray

A hydrocyclone fulfils two important functions: separating fine from coarse particles and producing an underflow slurry of a consistency that induces efficient grinding in the mill to which the slurry is recycled. Generally, the most efficient operation of a standard closed milling circuit requires the underflow of the hydrocyclone to have a narrow-angle underflow spray nearly at the point of roping, but not actually roping. An ultrasonic meter for measuring this angle has been used successfully in industry for control and optimization.

1.8. Particle size of milled product

Industrial online size measuring devices operate on principles such as ultrasound attenuation, laser diffraction or imaging and physical probing. These systems can give good results if installed, calibrated and maintained well. Their accuracy and reliability are very dependent on having representative and well-maintained sampling systems. Soft sensors that use flows, densities and other measurements can sometimes give accurate and more reliable derived measurements of size, but they do require regular calibrations. These soft sensors also eliminate the time lag between real and measured size changes that result with the physical meters. This time lag can be a severe limitation to fast and effective control. The best system uses a combination of both a soft sensor and a physical meter, with the use of the best features of both.

1.9. Grade

Online measurements of gold concentrations in various process streams would be good to have for control, but are generally not practicably possible for gold. This is especially true in respect of solids in tailings streams, where the measurement of grade would be most useful.

1.10. Cyanide concentration

Titration and electrochemical methods have been applied with success to measure cyanide concentrations in absorption and leaching vessels. They can give good indications of the *leaching strength* of solutions that contain multiple cyanide complexes, because they tend to measure the concentrations of those complexes that tend to be available for leaching gold.

2. THE BASICS OF PROCESS CONTROL

This section addresses some of the important common tasks and widely available tools needed for basic process control of gold plants.

2.1. Actuators

A control system influences the operation of a process by sending signals to actuators. The number and types of actuators determine how many and which variables on the plant can be controlled. For example, a variable-speed pump is invariably necessary in the control of closed milling circuits because of the need to regulate circulating loads as well as sump levels.

Although actuators are usually designed to act linearly, they often have some undesirable characteristics or there might be some unfavourable dynamics in the way the plant reacts to them. Where possible, good control strategies therefore have a local fast-acting control loop for each actuator that regulates a measurement of the associated plant input. In fact, inexpensive actuators with poor characteristics can often be made to give very good results when a fast-acting local loop can overcome its faults. This is particularly true of valves where there are associated measurements of flow rates.

2.2. Noise and signal conditioning

Process signals from measuring devices invariably have noise or other undesirable variations. Particular culprits on gold plants are nuclear-based measurements, mill power and variables derived from image processing. A common shortcoming on many plants is the lack of appropriate analogue filtering of electrical signals before they are sampled periodically by an analogue to digital converter. This introduces aliasing that transforms short-term signals and noise into what looks like long-term drift or low-frequency noise. Too much filtering of a signal can cause unwanted sluggishness in control loops and can sometimes obscure symptoms of a problematic measuring device.

2.3. Proportional-integral control

Proportional-integral (PI) feedback control loops are commonly used on gold plants. Because of the noisy measurements generally present on these plants, derivative action tends to cause too much actuator action and is rarely used.

Many PI controllers are poorly tuned and few people know or remember how to tune them properly. A ‘fiddle and test’ method of tuning often results in too low a gain and relatively too much integral action. This occurs because when a control loop appears to be too active, the operator’s natural inclination is to turn things down. This is effective in respect of the gain setting, but not the *reset* setting, which gives more integral action the lower it is. The integral action is generally not immediate-acting, so adverse effects are not seen immediately when it is set too high and the gain is made correspondingly small.

PI control is not always very successful. Problems can occur when there are adverse dynamic characteristics. A more advanced controller can handle the dynamics of long time lags introduced by solids-feed belts more appropriately. Multivariable interactions between plant inputs and outputs are often more appropriately dealt with by advanced control.

2.4. Hierarchy

Process control is best applied in a hierarchical structure that can be regarded as having several layers. The lower layers operate the fastest and are nearer to the plant itself, physically or conceptually. Higher layers depend on the lower layers and should only be operated when all the lower layers beneath them are properly functional.

The bottom layer comprises measurements, actuators and other hardware and software up to the provision of the lowest level of control loops. Typically, this includes functionality of either a programmable logic controller (PLC) or a distributed control system (DCS). The control here is mostly done with single-variable PI or ratio loops that have response times of not more than a few seconds. The bottom layer is where most faults in a control system commonly occur – inappropriate signal conditioning, electrical noise, earth loops, incorrectly chosen or installed measuring devices or actuators, faulty or inaccurately calibrated converters, incorrectly tuned PI controllers, etc.

The next layer up provides for fast stabilizing control, generally with response times of several seconds to a few minutes. The control loops here are generally more advanced in nature than those in the lowest layer and they typically drive the setpoints of the lower loops instead of the actuators directly. The dynamics of a gold plant's operation leads to a complexity that should have appropriate stabilizing technology implemented in this layer to deal with it.

Higher up is the layer containing optimizing control, where optimum setpoints for the layers below are determined. This optimization generally has response times of minutes to hours, and it is commonly a combination of automated optimization and operator-assisted optimization. The modern trend is for a complementary combination of both of these to be used, with the operator being assisted to understand and not ignore the automated functionality (Van der Spuy *et al.*, 2003).

The highest layer is where control and optimization is elevated to a plant-wide level and where it merges with management functions. Long-term interactions between plant sections are optimized in terms of profits and operational requirements. An enterprise-level management information system can be used to make managers the overall optimizing drivers of the plant.

2.5. Simulation

Advanced mechanistic dynamic simulators can give very good insight into what is required for the development of effective control strategies (Hulbert, 2003). They tend to have many states and parameters – often too many for online model tracking on real plants that have just normal measurements. Advanced mechanistic simulators are therefore used mostly for gaining an understanding of processes and for theoretical testing of process control. When the basis of a control strategy has been determined, the advanced mechanistic simulator is usually best put aside. The dynamics of the plant are then measured in perturbation tests, and models more amenable to controller design are then fitted.

3. ADVANCED CONTROL AND OPTIMIZATION

It is increasingly being recognized that the use of just PI controllers and other simple control elements is inadequate for good stabilization and optimization. For example, it has been shown by experimental tests on a number of flotation plants, including a gold plant, that advanced stabilizing control can yield about 1% more recovery than conventional PI control. This is because conventional PI control of flotation tends to transmit and amplify disturbances between flotation banks instead of eliminating them. The non-linear response of tailings grades then causes increases in its average values, and hence reduced recoveries.

A modern trend in advanced control is the use of artificial intelligence (AI). Common AI methods include neural networks, expert systems, fuzzy logic and genetic systems. There is no widely accepted answer to the best choice of these for gold plants. Whereas some people have the view that AI systems mimicking human intelligence will ultimately give the best control, humans and AI systems are sometimes much less inefficient at dealing with complex problems than known technical solutions that have been customized to solve them. The simple answer is to use good technical solutions where they are known and can be implemented, maintained and accepted by operators; and otherwise to use good AI techniques appropriately for unsolved technical problems, the implementation of non-technical solutions and for softer operational and psychological issues.

By its nature, advanced control and optimization on gold plants generally requires people or organizations with specialized expertise and experience in such applications. This is true whether the advanced techniques involve general AI, or process-specific technical solutions, or both. Individual plants seldom have specialists in these advanced technologies, so a partnership with a technology provider is commonplace. Such a partnership should involve a concentrated effort for the initial implementation and decades of less intense maintenance and upgrading subsequently.

3.1. Solids feed control

Most gold plants have some potential problems with the control of solids feeds. These can include the adverse effects of ore segregation, non-linear or erratic actuator dynamics (especially vibratory feeders), moisture content, conveyor-belt dynamics and blockages. All of these issues are readily solved by appropriate advanced technologies (Louw *et al.*, 2003) that produce the best possible results. Fig. 1 shows industrial results obtained from the replacement of conventional PI control with appropriate advanced control. When there are multiple withdrawal points from an ore silo, blending can be maximized, or sometimes segregation can be exploited to optimize short- to medium-term grinding conditions. Invariably, a fast and noise-free response of the actual solids feed rate to its setpoint is required for good higher-level control, *e.g.* for the control mill load.

3.2. Crusher plant control

Crushers have relatively fast dynamics. Screens, too, have quite fast dynamics. As a result, these two processes can be essentially regarded as instantaneously responding units, connected by conveyor belts to other units

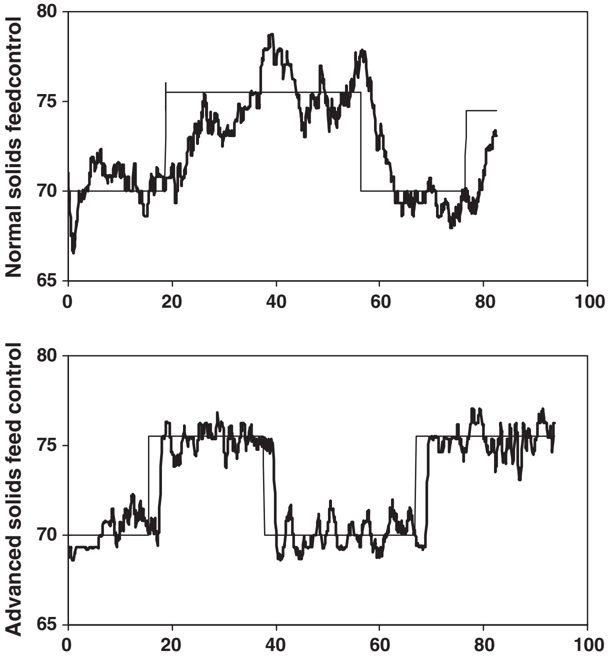

Fig. 1. Comparison of mill solids feed with conventional and advanced control.

or solids storage bins. Control can be applied in a strategy that allows particularly for the dynamics of conveyor belts and for constrained control and optimization. Attention should also be given to start-up and shutdown sequences and their control.

3.3. Mill circuit control

In the early 1980s, successful multivariable control of industrial milling (Gossman *et al.*, 1982) brought recognition to the fact that milling circuits have complex interactive dynamics that can be modelled and controlled very well by advanced methods. For operation away from the influences of process limits, good multivariable control is easily implemented by many of the advanced methods that are now standard.

Because the optimum operation of milling circuits is almost invariably near process limits, optimum control requires a multivariable controller that has switching control strategies, for use when various combinations of process inputs and outputs change between being constrained and unconstrained. Model predictive control (MPC) is a good general technology for this, but it is complex, cumbersome and less reliable in its general form, so specialist adaptation should be applied to exploit specific characteristics of milling circuits (Muller *et al.*, 2003). A switching control strategy (Hulbert, 2001) has been developed to allow for easy specification and tuning. It provides for controlling process outputs to setpoints, minima or maxima, or combinations of these. A typical list of setpoints for a simple closed milling circuit would be setpoints for sump level, product size, circulating load density or underflow angle and cyclone feed density or flow. Minima and maxima could be set for mill power, sump level, product size and cyclone feed density. Priorities can be set for the various setpoints and limits for when not all of them can be satisfied.

Besides handling the process limits properly, the controller should optimize the operation of a milling circuit while controlling product size to a setpoint. The setpoint used for product size itself might need to be adjusted to give a required long-term solids throughput. In autogenous milling, conditions inside the mill might need to be made such that preferential grinding of either the fine material or the coarse ore takes place.

3.4. Thickener control

The most common process controllers used in thickening are those for thickener underflow density and flocculant addition. The thickener underflow density is controlled to a setpoint by a variable-speed pump. The setpoint can be manipulated in a plant-wide optimization scheme that minimizes gold losses and prevents any undesirable bottlenecks. The flocculent is usually added in ratio to the flow of solids to the thickener. If unknown, this flow of solids can sometimes be estimated from a *smart sensor* based on measurements of an upstream milling circuit.

3.5. Carbon-in-pulp and carbon-in-leach control

Carbon-in-pulp (CIP) and carbon-in-leach (CIL) are widely used for the extraction of gold by the use of cyanide. Pulp levels are easily controlled, usually mechanically, by means of overflow weirs. Carbon transfer is done in batches or, in some cases, continuously. The long time constants in CIP and CIL plants make it possible for carbon-related measurements from hand samples to be used. However, cyanide concentrations are best determined and controlled automatically and with minimum measurement delays, as they reflect faster process variations and disturbances, and these need to be reacted to quickly. The carbon and cyanide inventories should be optimized to give the optimum financial performance of the plant as a whole. The associated index of performance should include the income from gold recovered minus the costs of cyanide, carbon and any other reagents (such as lime and oxygen) used.

3.6. Flotation

A flotation plant should have advanced stabilizing control of its pulp levels (Hulbert, 1995) if it has three or more flotation banks or columns operating in a

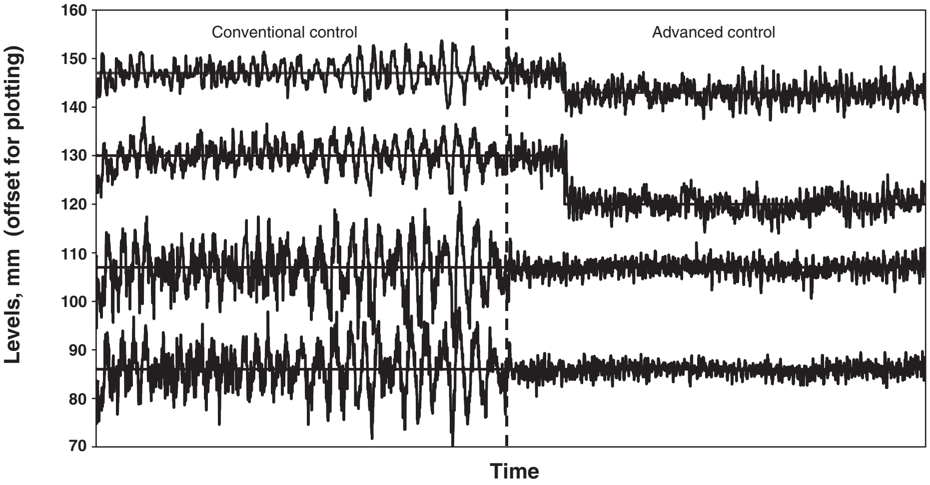

Fig. 2. Comparison of conventional and advanced flotation level control.

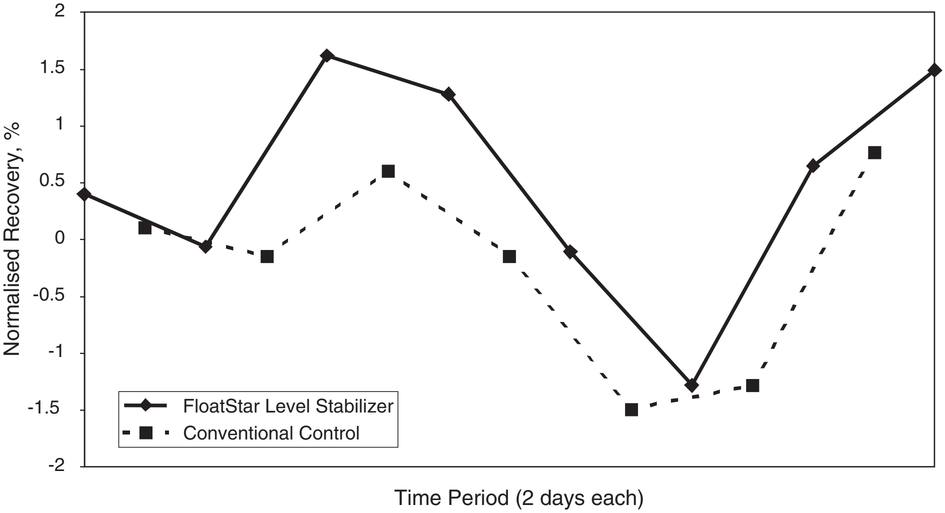

Fig. 3. Measured recoveries in alternating periods of conventional and advanced level control.

cascade. This is because conventional PI control operates poorly on the related third- or higher-order dynamics of flotation plants and simply transmits disturbances between stages instead of eliminating them. Fig. 2 shows a comparison of conventional and advanced control of flotation levels on an industrial circuit.

The advanced stabilization of levels, alone, can produce measurable improvements in recovery of around 1%, as is illustrated by some industrial results in Fig. 3. An added benefit of fast-acting stabilizing control is the

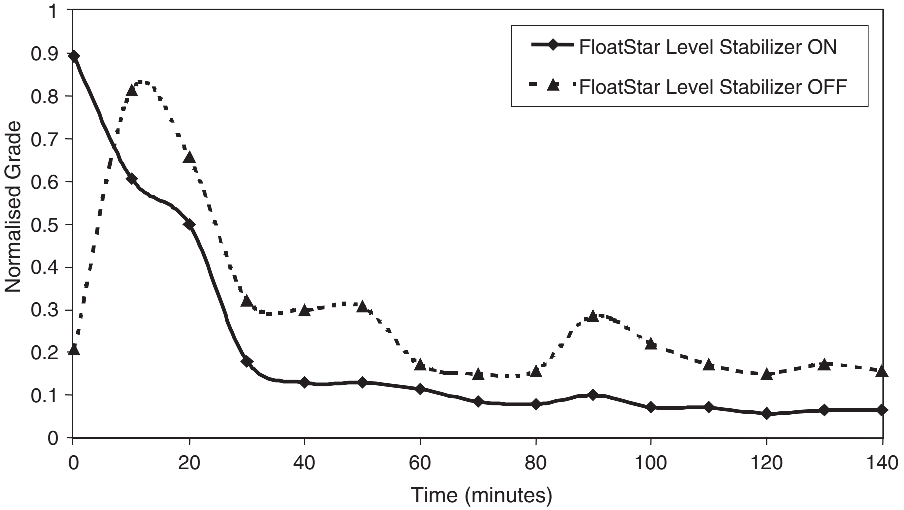

Fig. 4. Faster and better settling after start-up of a flotation plant with advanced level control.

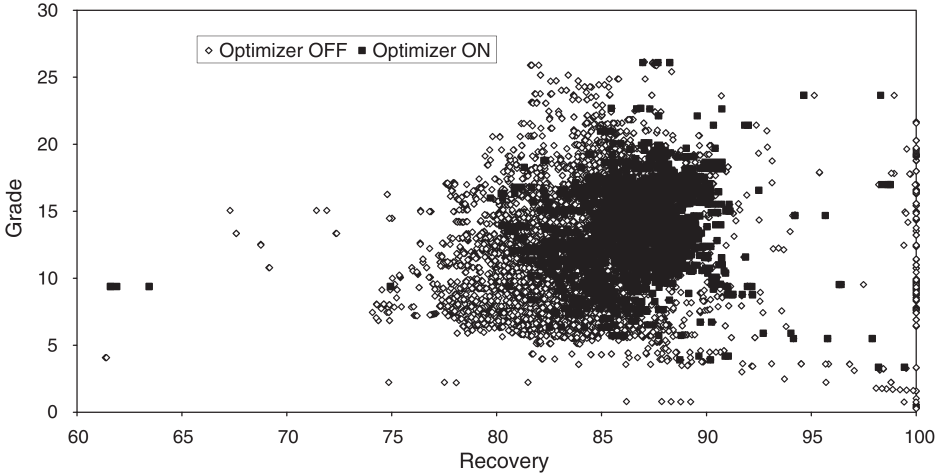

Fig. 5. Comparison of flotation operation with and without optimizing control.

reduction of losses of valuable material during start-up. Fig. 4 shows industrial results to illustrate this.

Where there are cleaner flotation stages, flow rates and residence times should also be optimized dynamically, while the levels are being controlled (Singh *et al.*, 2003). Fig. 5 shows improvements in the grade–recovery relationship on an industrial plant with optimizing control implemented above stabilizing control.

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I.4 *Closure and Rehabilitation*

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Mike D. Adams (Editor)

Chapter 10

Closure and rehabilitation of gold-processing plants

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While this chapter derives primarily from an Australian experience base, the principles are generic. The reader is referred to the relevant state and government legislation to augment the information herein.

1. PROCESS CLOSURE AND CLEAN-UP

Each mining operation goes through a number of phases in the course of its life, the final one being that of closure, abandonment and rehabilitation back to an appropriate landform and land use. Essentially, it is an exercise in risk management to achieve outcomes appropriate to stakeholder objectives and expectations. The strategy should include consideration of likely outcomes within the context of the potential for (i) an operation to reopen at some future time subject to future exploration success and (ii) total closure, abandonment and rehabilitation in the event that mining and exploration leases are sterilized. Ideally, a closure strategy and plan should be completed

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at the earliest opportunity in the life cycle of the operation. In this chapter, we deal with one section of a mining operation under closure appropriate to the topic of this book, *i.e.*, process closure and clean-up.

There are a number of considerations to this:

- Maximizing recovery.
- Preservation of assets and care and maintenance.
- Removal of infrastructure.
- Rehabilitation of the site, tailings storage facility and associated infrastructure areas.

Each of the above requires comprehensive planning to achieve the best outcome. Closure and clean-up tasks should be identified well prior (*e.g.*, 12 months) to the commencement of closure and included in a plan, which has the tasks scheduled and is fully resourced with labour, materials, equipment and consumables, with a budget appropriately provisioned. Commencement of the planning process well prior to the closure date permits refinement and testing of the strategy and plan, which will ensure a higher chance of a successful result.

In the authors' experience, residual gold can remain throughout the crushing, milling, leaching and refining areas of a gold plant. Most of these areas are relatively easily cleaned with high-pressure water cleaners, needle guns, jackhammers and concrete scabbling units. Some areas are particularly difficult to remove the residual gold, as it is smeared or impregnated into the substrate, *e.g.*, rubber mill and pump hopper linings. In these instances, chemical leaching may be appropriate or one may consider contracting one of a number of gold-recovery operators ('scavengers') for these tasks. Typically, these contractors will perform the task for a percentage of the gold recovered and one needs to be familiar with the degree of difficulty of the gold recovery tasks under consideration when negotiating the terms – there have been numerous easy ounces delivered up unnecessarily.

2. RELOCATION AND SALE – OWNER'S PERSPECTIVES

An operation may reach the point where the ore reserves are depleted and the surrounding tenements have been sterilized with respect to exploration and hence, no further mining and processing is possible. This raises the question of what future use the assets may be put to and a decision must be made as to the most beneficial use or disposal of the processing plant and infrastructure:

- Relocation
- Toll treatment

- Sale
  - As a whole to another party.
  - Deconstructed and piecemeal sale.

When considering relocation or sale of a process plant, questions which must be answered include:

- Could the plant be utilized elsewhere in the organization (if the owner has other operations)?
- Could leaving the plant *in situ* and toll treating yield better value? This depends on the underlying tenement situation and availability of suitable ore producers.
- Could deferring the sale until the commodity prices rise yield a better result?

Aspects that affect this are the condition of the plant and whether it is possible to economically deconstruct and rebuild the plant on another site. The distance to be transported may be significant enough to impact the economics. The all-important consideration is whether the plant is of a capacity that is suitable for another operation. Collectively, the answer may be that the economics are against it and constructing a new plant is the more effective solution.

In terms of toll treatment, factors which impact may include:

- Access to potential clients closeby
- Suitable processing route for client ores
- The economic margins of potential clients, which may be affected by:
  - Ore grades
  - Metal recovery
  - Haulage distance
  - Client financing.

The option of deferring a sale until the price-cycle rises, to capture a better result, needs to be analysed in terms of the future market expectations and the likely increase in the magnitude of the expected sale price, taking into consideration the cost of keeping the plant under care-and-maintenance to maintain plant condition and value. This in reality may be a significant gamble. Availability of other plants at the time of sale will also significantly impact on the supply- and-demand equation. More favourable prices are likely to be realized when there are few second-hand plants and little second-hand equipment available.

Once a decision has been made to sell, the main concern is attracting a good price and establishing mutually acceptable sale terms. Price expectations are then affected by:

- Plant condition and structural integrity.
- Remoteness of the location, since the buyers will need to pay for dismantling and transport.
- The age of the plant and likelihood of reassembly problems (as well as any shortage of spares).
- Plant capacity (particularly grinding capacity) since this will affect the target market.
- Market conditions that affect the demand for infrastructure (*i.e.*, commodity prices, exchange rates, and if the new plant is bought from overseas, the supply of second-hand plant).

Ultimately, the price realized is significantly influenced by a buyer's needs. These needs may include:

- The plant must contain the right unit processes.
- The optimal capacity for their operation.
- The need to establish an early cash flow due to financial constraints.
- Loan-repayment obligations.
- Hedging obligations.

Assessing what price a plant may bring is not that easy and the true value realized may be significantly different to expectations and often in the negative. There will be the residual written-down value of the original capital cost of the plant at the time of closure. This is typically an unreliable indication of value as the rate of depreciation may have been incorrect and it in no way reflects market forces. Obtaining a valuation from accredited and licensed second-hand equipment valuers will provide an indication of what may be expected; however, experience has shown that these tend to be on the high side. Tendering and auction sales ultimately provide the answer, as they are a reflection of what the market is prepared to pay at a particular point in time. It is wise to ensure that at auction there is a reserve price and with tenders a clause under which the owner shall not be bound to accept the highest offer or any tender. These protect the owner from being committed to a sale if the price offered is considered low, and permit the opportunity for subsequent negotiations to realize an acceptable price.

It is useful then to have a prior knowledge of what is happening in the industry in terms of similar projects closing down and new projects coming on stream over the relevant time frame. This then permits potential buyers to be identified and may help make decisions in how the sale is to be executed. Sale methods may include:

- Negotiated private sale
- Auction
- Tender
- Third-party vendor.

The decision to sell by one method or another may depend on having the relevant skilled resources within the organization or whether they need to be hired in. In the event that there is already an interested buyer, a negotiated sale may be able to be completed in-house. In the event that assistance is necessary from a third party, then their credentials and performance must be researched thoroughly before making an appointment. It is well to keep in mind what fees may be payable, and which may be on a percentage basis or a fixed dollar value. Methods sale such as auctions, by tender or through third-party vendors may take considerable periods of time depending on exactly how they are structured. If time is a vital factor then it must be an essential clause in any contract of engagement.

3. RELOCATION AND SALE – THE MARKETING MANAGER'S PERSPECTIVES

In determining value retained in plant, managers can only find answers attainable through knowledge of the market prices that are currently achievable on a given date. Managers within firms that deal with mining plant and equipment for local, national and international mining companies are constantly seeking this information and remaining in touch with market values and fluctuations across the globe.

Options for sale (marketing options) are often determined in conjunction with the owners of the equipment as to their specific requirements. Options include auction sale, tender, private negotiations or expressions of interest. Within all these options special considerations include safety, time frames, age of equipment and site location.

Methods and costs of dismantling are determined by the age and saleability of the plant. Reverse construction, manual demolition and mechanical demolition are options that can be assessed, and again this depends on the condition or value of the equipment to be disposed of. The utilization of demolition shears and grapples can be combined with most of these options. Safety is always a prime determination in the method that ultimately should be used. Thorough planning for safe relocation and delivery of valuable components by either shipping or road is of utmost importance and enables companies to gain maximum value from all components and all recyclable scrap.

4. SCRAP, RECYCLE AND RE-USE

All items of a plant are assessed for their potential value and re-use, with consideration given to location and costs involved to relocate. Often the greatest value is achieved via public-auction processes, which allow the greatest number of potential purchasers to participate in the sale.

Key stakeholders in preparation for auctions can include federal, state and local government officials, landowners, local communities, company shareholders, staff and the general public. Safe working environment is always a first priority in handling any dismantling of plant and equipment on a mine site. During that decommissioning, the need to minimize environmental impact to flora and fauna is paramount. All respect must be given to other forms of land use as well as users of land near the mine.

In assessing scrapping values, the amount of scrap value on a particular site is usually determined by world prices in scrap metal. At present, some 95% of all scrap metal in Australia is currently exported for reprocessing. Fluctuations in obtainable prices can determine the amount of scrap that can be removed from any individual site.

Properly marketed and packaged disposal of obsolete mine equipment offers considerable value and unique opportunity to other mining companies (especially junior miners). Alternative industries, private industry and agricultural concerns can also greatly benefit by purchasing used equipment, especially where the purchase of new equipment is not financially viable or available.

The reasons for mine closure can vary, and can include the age of plant and equipment, depletion of available viable ore or social, political or environmental impact. This means that a large percentage of the plant and equipment can still potentially have a long useful life in the same or other industries.

The opportunities to re-use and recycle are only limited by the imagination of the people. For instance, during a recent diamond mine decommissioning, polyethylene pipe from the mine watering system was on-sold to local agricultural plantation owners, and quantities of excess steel was sold to be utilized by local cattlemen in building cattle yards and sheds.

5. CONSIDERATION OF HERITAGE VALUES PRIOR TO CLOSURE AND DECOMMISSIONING

There is a considerable and growing community interest in our heritage. This is particularly true of our mining past, where the engineering feats and hardships endured by workers often engender a sense of awe. The modern mining industry too, has its share of community interest, although it can be reluctant to advertise its presence. At one modern gold mine close to residential areas, the first *open day* attracted 4,000 inquisitive visitors.

Some goals of rehabilitation are to make a site safe, contain potential contaminants and stabilize landforms. While these are overriding considerations, in the authors' opinion, it is also appropriate to leave a *monument* to the mine and people who worked there. Often, this can take the form of concrete crusher or mill foundations upon which can be attached a plaque with details of the mine that was. Schemes that are more elaborate have included a marked walk trail around an old plant site, and at another site, interpretative plaques describing the operation and with images of the people and plant during operation.

Consideration may be given within the decommissioning strategy to heritage issues depending on the operation's:

1. Uniqueness
2. Novel technology
3. Infamy
4. Life
5. History
6. Economic importance to the area, state or country.

The mining industry has been a significant pillar in the economic development of most nation states, in particular through the Australian and Californian goldfields. Original mines that were constructed to build cities, provide coal and building materials are often listed under Heritage Acts. It may be argued that with so much mining currently being undertaken that it is not necessary to make any provision for heritage as the equipment and the methods are common. Our ancestors in mining may possibly have shared this sentiment; however, who cannot be moved to some slight wonderment when viewing some of the old equipment used in the mining industry in previous decades and centuries. The stamp mills, the dry blowers, the staved pipes or the timbering underground and the beam pumps and one should never forget the conditions under which this took place as evidenced by the myriad of photographs of that era to be found on many a hotel or restaurant wall in our current mining towns or on the headstones in the old cemeteries. All of this tells a great and precious story of our development. One wonders whether the miners of the future, another 40 or 50 years hence, will likewise be of similar sentiment and maybe we should be more proactive in regards our heritage and be proud of what we have achieved as it is a measure of who we are.

During closure planning discussions with local and regional stakeholders – the issue of what a mining operation will leave behind is a major focus. It is of paramount importance that mining operations, in iteration with communities, take the opportunity to consider heritage values and if possible design Mine Closure programmes that leave safely decommissioned sites that have value designed into the closure for the benefit of local history and heritage.

6. INFRASTRUCTURE REMOVAL AND SITE DECOMMISSIONING

A time is reached in the life of a mining operation where a condition results in the need to remove infrastructure. This may be due to plant upgrading or replacement or ore reserves being exhausted and subsequent mine closure. Ideally, appropriate preparations for eventual decommissioning are made from the time that the mine was initially developed. This planning idea is becoming a standard condition in mining, with many financial and regulatory organizations demanding this plan prior to financing or approvals being granted to mine.

A removal strategy is evaluated in line with the stakeholder's requirements and desired outcomes. A number of approaches may be taken including:

- Appointment of a third-party specialist equipment vendor to act on behalf of the principle
- Disposal by auction
- Contracted removal by a specialist demolition company
- In-house by the owner's company
- Sale of project and facilities (see Section 2).

Each may be varied to suit the principle's requirements with differences typically being:

- timeframe to completion;
- magnitude of returns achieved or cost to principle;
- risk management profile;
- extent of effort required by the principle; and
- removal strategy that takes heritage issues into account.

Carrying out these types of works is essentially an exercise in risk management, *i.e.*, removal of uncertainty of achieving the desired outcome. Early preparations in developing the removal strategy and planning and scheduling the work with full resources available will secure a satisfactory result. As such, there are a number of key components that need to be considered and addressed.

Safety in performing the works is a critical concern considering the type of work involved where people may be using gas-cutting equipment, lifting and rigging, working at heights, residual chemicals in pipework and tanks and working with different types of mobile equipment and haulage transports. It is essential that the personnel be focussed on carrying out the work with safety as a key priority. There must be a safety system and written safety management plan embodying duty-of-care principles approved by the company and communicated to all personnel involved prior to the commencement of work. The involvement of the employees is seen as a key factor in underpinning the work being carried out safely. A safety management plan may address the following as a minimum:

- Safety policy and commitment.
- Communication of the policy.
- Conduct of daily prestart meetings.
- Conduct of safety meetings (frequency/minutes).
- Inspections (equipment/work area/vehicles, *etc.*).
- Defect reporting and correction/repair.
- Training – including inductions and other training as necessary in safe operating procedures, good housekeeping and hazard recognition.
- Authorization of operators.
- Risk assessment – for unusual tasks, working at heights, rigging or when experience is limited.
- Hazard identification.
- Job safety analysis.
- Incident and accident investigation, management and reporting.
- Allocation of responsibilities for occupational health and safety (management/safety officer/safety representative/employees).
- Emergency preparedness and procedures.
- Workplace health and safety regulations.
- Use of protective equipment.
- Isolation procedures.
- Work permit system.
- Working in confined spaces.
- Working with hazardous substances.
- First-aid facilities.
- Fire extinguishers.
- Contractor and subcontractor management.
- Consistency with the company's health, safety, environment and community policy.
- Audits and reviews.

Protection of the environment from damage of any nature is another area of significant importance. Personnel engaged in the work must be fully aware of the company requirements imposed at the site in relation to environmental protection and conservation and abide by these conditions at all times, including:

- Minimizing damage to the environment.
- Restricting movement of equipment and personnel to work areas and to defined access roads.
- Preventing the entry of substances into any watercourse or ground-water aquifer, which may be deleterious to life.
- Complying with all relevant laws controlling the discharge of liquids, gases or particulate matter into the environment.
- Accepting full responsibility for any pollutant or waste material of whatever nature arising out of performance of the work.
- Preventing spillage of any hydrocarbon or liquid other than water in any part of the works site.
- Not causing or permitting damage or injury to any flora or fauna.
- Not permitting fossicking on the mining lease by any unauthorized person.
- Environmental audits by the Company's Environmental Representative.
- Environmental rectification works deemed necessary to be carried out.
- Not breaching the environment protection or environmental rehabilitation requirements of the mining tenements.
- Appropriate handling and disposal of all refuse and waste.

Planning and scheduling of the work with full resources available is seen as critical to the success of completing the work with safety, on time and budget and within the stakeholders' requirements. The work program should be developed identifying the demolition methods and the timeline for each of the major activities and the labour requirements, covering:

- Mobilization of plant and equipment
- Site establishment
- Demolition work operations for each area of the site
- Demobilization
- Detailed execution plan
- Establishment of appropriate infrastructure for access, equipment lay down and the work areas
- Management, supervision and control of the work in terms of safety, environment, quality and personnel performance
- Prepare work schedules with which to monitor progress against plan in order to drive the project to completion.

A significant component to planning is the *methodology of the deconstruction.* Where crane lifts are a component, the analysis and planning of these lifts is paramount. Access to the construction drawings and the weights of the equipment and structural components and modules is needed. If not available, then weights must be determined for the lift analysis and in any event, allowance must be made for the likely increases due to adhering or contained process solids or liquids.

Engagement of contractors for the deconstruction requires considerable effort with respect to risk management. A suitable contract (in accordance with Australian Standards, by way of example) for the work needs to be developed with a detailed scope of work and tendering process established. Potential deconstruction contractors must be identified and invited to tender for the work. Factors to select candidates may include:

- Relevant experience
- Demolition licence
- Appropriately skilled personnel
- Safety system
- Drug and alcohol policy
- Past safety performance
- Appropriate equipment for the work, *e.g.*, mechanical shears *vs* gas cutting
- Job performance record
- Industrial relations (IR) record
- Financial capabilities.

The tendering process may include a site visit to view the infrastructure and provide the opportunity to assess the job. Sufficient time must be provided for the proper preparation and evaluation of tenders.

Access to the site must be controlled to prevent inappropriate entry to the site by company personnel, the general public, and local land-users of all kinds. Hard barriers such as bunding and security fencing must be installed with appropriate signage warning of the personal risk. Entry procedures to the site need to be set up with the company and contractor personnel for the period of the deconstruction.

Prior to the commencement of work, a sweep of the site may be undertaken to identify the presence of *hazardous materials* and chemicals and their locations. Where the identity of materials or residues are unknown, samples should be collected taking proper precautions and sent to specialist laboratories dealing with such materials, *e.g.*, asbestos materials, synthetic mineral fibre insulation, hydrocarbons, maintenance chemicals (*e.g.*, paints, adhesives, lubricating and dewatering sprays, *etc.*) and processing chemicals (*e.g.*, cyanide, acids, caustic compounds, *etc.*). Where possible these materials are best removed prior to the works commencing; where this is not possible the plans with procedures and job safety analyses ought to be prepared and the jobs scheduled in the work program.

It is essential that *services are isolated* in advance of deconstruction, including:

- Power reticulation and generation systems
- Water reticulation systems
- Compressed air reticulation
- LPG or natural gas reticulation
- Oil and fuel reticulation systems.

All isolations need to be of the *hard-barrier* type; where the service is provided by a public or independent utility, the isolation should be carried out by the utility disconnecting the service at the *boundary fence*. Water, compressed air, gas and hydrocarbon reticulation systems should have stored energy released and the lines emptied of their contents in the proper manner. Other sources of contained energy that need to be released may include pressure systems associated with grinding mill bearing lubrication, crusher hydro sets, *etc*. All energy sources should be *tested for dead* prior to commencement of decommissioning.

7. CLOSURE PLANT SITES – CONTAMINATION AND RISK

Mining and processing operations have a propensity to cause some contamination of surrounding and underlying ground (soil) and water resources (surface water and/or groundwater). This is particularly the case where plant has been in operation for many years prior to the advent of the relatively strict environmental controls and safeguards we see today.

In some jurisdictions, where environmental regulation is well advanced, there are specific definitions of the word *contaminated* and there are onerous legal requirements for the assessment of contamination and undertaking risk-based corrective action (remediation). In less regulated jurisdictions, the responsibility to assess and remediate contaminated ground and/or water resources is more up to the discretion of the lease or land-holder and corporate responsibility. In either case, the cost to conduct an adequate assessment and remediation could be very significant, and is likely to present an unwelcome surprise at plant closure.

The activities that can cause contamination may include:

- exploration activities;
- minesite construction work;
- mining operations;
- ore processing *in situ* and *ex situ*;
- tailings storage; and
- waste handling and disposal.

Typical contaminants associated with the above activities include:

- fuels and lubricants;
- drilling muds and additives;
- workshop wastes (*e.g.*, metals, rubbish, oils, coolants, solvents, paints, batteries, sandblasting detritus, acid and caustic materials);
- construction and insulation materials (*e.g.*, asbestos);
- ores, overburden and waste rock (depending on composition, potential for acidification, leachability and compatibility with the area in which it is handled and placed);
- chemicals used in the processing of ores;
- by-products of the ore-processing activities; and
- on-site waste disposal (landfills and other dumps).

The risks of each of the above contaminants being present at a minesite generally increase with the age of the operation because historical operations may not have operated to current environmental standards. It is also common for the layout of minesite and minerals-processing operations to change over time in response to expansion of operations and changes in process so it is essential to assess the potential for historical operations to have caused contamination in the past.

Current and historical operations may be associated with contamination concentrations such that there may be material risks of impacts to:

1. *water quality*, such that concentrations:
   a. are no longer potable;
   b. no longer meet stock watering guidelines; and/or
   c. present a risk to aquatic ecology, and
2. *soil quality*, such that concentrations:
   a. in soil or dust exceed human health thresholds;
   b. are phytotoxic, and/or
   c. present a risk to ecological functions.

Under the assumption that some form of remediation is required at plant closure, it makes sense to commence an assessment of the potential contamination risk areas as early as possible in the life of the plant. Once identified, the risk areas can be assessed and an appropriate programme to mitigate the risks can be devised. Such a programme could include:

1. Engineering solutions to avoid or minimize the potential for spills, leaks, and other discharges.
2. Modifying procedures to reduce the potential for discharges.

3. Training and education of all personnel to ensure that any discharges are subject to incident reporting and that the discharges are mitigated and subject to remedial action as necessary.
4. Commencing targeted investigations to assess the presence and extent of potentially contaminated areas.
5. Progressive remediation of identified contaminated areas.

Without a planned contaminated sites management programme in place at a minesite during operations, it is a considerable liability to plan, cost and conduct an appropriate assessment and remediation of contaminated areas – at the decommissioning phase. Mine owners are encouraged to address this issue as early as possible in the operations phase to avoid difficulties in decommissioning and to avoid closure complexity and potentially large liabilities.

8. FINAL LAND USE AND REHABILITATION – PLANT SITES

In the final closure of plant sites, the mine owner makes reference to final land use agreements and to meeting the original approval commitments to closure and rehabilitation. Plant areas are generally a small component of a larger area of open-cut disturbance that provided the ores for extraction. Underground mines, however, are often the reverse of this, with the plant, processing areas and tailings storage facilities being the focal area for rehabilitation.

The process of generating post-mining land use options primarily entails consideration of factors such as climate, topography, soils and adjoining land use. Stakeholder engagement through community consultation on the specific issues of post-mining land use with neighbours, local authorities and special interest groups is also a fundamental part of the process. Involving the community in deciding decommissioning options assists in focussing on the long-term economic and social sustainability of communities associated with the mine.

For each site to be rehabilitated, a prime question that should be asked is "is there any purpose that this site could be used for after mining that would be of benefit to the local community and/or the environment?" The application of the concept of *sustainability* is important, so that the chosen and ongoing use continues to be beneficial and does not become a liability (within best predictions).

In some cases, options for ongoing land use near a plant site may be limited due to economic, legal and technical constraints and there may be a potential risk in relation to ongoing final land use. For example, where deep voids remain with a surrounding zone of instability, it may be inappropriate to consider options that would attract people into the area, such as a visit to a *heritage* plant site. The first priority must always be to protect public health and safety and environment, by using safe and responsible closure practices.

8.1. Relinquishment

Throughout the world, the concept of satisfactory minesite relinquishment is complex and this matter is discussed in more detail in Section 5. In Australia, for instance, most mining operations are conducted under a form of mining tenement that can co-exist with other forms of land titles. For example, many mining operations are conducted on private freehold land, pastoral leases and reserves. At the end of an operation, it is usually the intention of the company to relinquish its title over the land where responsibility for the decommissioned site reverts to the government or landholder.

Company relinquishment objectives are to reach a point where the company has met agreed completion criteria to the satisfaction of the responsible authority. It is important that a responsible authority is identified and held accountable to make the final decision on accepting closure. The responsible authority will make a judgement on the achievement of the agreed completion criteria after consultation with other involved regulatory agencies, including the future land manager (ANZMEC/MCA, 2000). This applies to both financial securities and tenure over the mining area.

Relinquishment may be a staged process as progressive completion criteria and/or benchmarks are achieved. A sufficient period should have elapsed to demonstrate the stability of the site. It may take several years (or even decades) of monitoring to establish whether a stable and satisfactory quality or state exists at a decommissioned minesite (Environment Australia, 2002). Under some circumstances, a company may be required to retain some ongoing liability under broad environmental or civil laws for specific aspects of the operation for an indefinite period (*e.g.*, contaminated sites).

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Chapter 11

Closure and rehabilitation tailings storage facilities

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While this chapter derives primarily from an Australian experience base, the principles of closure can be considered generic, and the author draws upon international literature. The reader is referred to the regulatory guides and legal information from relevant state and governments where any particular facility is located, to augment the information contained herein.

1. STANDARDS AND CLOSURE CRITERIA

In this section, we will discuss Tailing Storage Facility (TSF) closure both as a subset of general mine decommissioning, and where appropriate focus on the unique challenges of closing tailings storages.

Mine decommissioning and closure is the process of shutting down a mining operation with the broad objective of leaving the area in a safe and stable condition that is consistent with the surrounding physical and social environment and does not need ongoing maintenance. The mine area may also be suitable for alternative, post-mining land uses depending on site-specific circumstances (Environment Australia, 2002).

Mine decommissioning usually occurs at a point in the life of an operation where the economic recovery of minerals has ceased. However, the overall mine decommissioning process can be integrated with the overall mine operation planning process. In other words, the mine can be designed and operated with a continual review on closure outcomes. While new orebodies and mineral resources are constantly being discovered through exploration,

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the reserves contained in any particular deposit on which a project is based are finite and closure is inevitable.

Factors contributing to cessation of mining activities include:

- depletion of mineable reserves;
- changes in market conditions;
- financial viability of the company; or
- adverse environmental or political conditions.

Standards and completion criteria are the focal point for mine decommissioning. Best Practice standards and completion criteria are those that are clearly understood and agreed by the company, the regulators and other stakeholders. Relevant standards for mine decommissioning ideally need to be developed on a site-specific basis based on the nature of the operation and the environment in which it operates. However, this approach also needs to be underpinned by generic regulatory standards to provide the community with a degree of confidence that minimum acceptable outcomes will be achieved. Companies should seek to apply the same standards universally, exceeding the local standards if these are below the standards the company applies in their home country.

Standards and completion criteria must be finely balanced between flexibility to allow changes in circumstances while being specific enough to provide certainty through measurable outcomes. Effective consultation between a mining company, the community and regulatory authorities is the best means of developing standards that are both appropriate and achievable. This also ensures that there is a broad agreement for both the ongoing land use objectives and the basis for measuring the achievement of the objectives (ANZMEC/MCA, 2000).

Through most of the late part of the 20th century, much of the focus for mine decommissioning was on rehabilitation. During this time, a number of national and international forums began to focus on the issue of *Sustainable Development*, based on the concept of meeting the needs and aspirations of the present, without compromising the ability to meet those of the future. The debate was also broadened through such forums with the closer involvement of various non-government organizations and community representatives. The present mining industry has been influenced by the awareness of the massive mine closure liabilities in the USA and Canadian mining industry and the subsequent development of the *Superfund* legislation.

Realization of the need to plan for decommissioning has become an integral part of mine planning and operations management and became more prominent through the 1990s and is a common practice in most current operations. However, there are still many legacies of past practices that will need to be accommodated by the society in coming years.

2. CLOSURE PREPARATION, PROVISIONING AND PLANNING

There is a range of factors to be considered when preparing to decommission a TSF. The hostile nature of tailing stored in many facilities requires that decommissioning and subsequent rehabilitation is carefully planned and executed. Environmental or climatic conditions must be considered and potential problems likely to affect the long-term integrity of rehabilitation works be taken into account (Lacy and Ward, 1998).

Mine closure (hence of TSFs) should not be an "end-of-mine-life process" but should be integral to "whole-of-mine-life" if it is to be successful. Planning for closure should commence at the prefeasibility phase of an operation. In this way, future constraints on, and costs of, mine closure can be minimized, post-mining land use options can be maximized and innovative strategies have the greatest chance of being realized (ANZMEC/MCA, 2000).

The most important principle to maintain when developing a TSF at the design stage is to motivate project planners and tailings consultants to design and engineer out long-term liability, and with the "end in mind", that is, of the known reserves. Company planners that have maintained this attitude have considerably improved recent tailings construction in Australia. It is also apparent that the leading consultants are encouraging clients to accept designs that particularly avoid the use of tailings in upstream lifts, particularly when run of mine waste is available and alternatively designing armoring for those TSFs whose walls are made of tailings with underground development waste post-construction.

The general approach to developing decommissioning plans allows site-specific factors to be taken into account. This approach also recognizes that the plans will evolve throughout the life of the mine to accommodate changes in the project and increased knowledge and understanding of the local environmental conditions.

The Australian approach differs from some "command and control" type regulatory frameworks where more prescriptive decommissioning outcomes are imposed at the time of initial project approval. While the Australian approach allows for more flexible outcomes, it also requires greater commitment by the company to provide sufficient resources, undertake necessary studies and implement appropriate progressive closure plans. Greater diligence is also required on the part of regulators to monitor the progress of the decommissioning works and ensure acceptable outcomes are achieved (Environment Australia, 2002). Time will tell if this approach will work – given the leading members of the mining industry's commitment to 'sustainability', this is possibly the correct policy at this time.

Financial provisioning is crucial to Best Practice mine decommissioning, and to ensure that there are sufficient funds available to close an operation – especially in later years of the mine life when revenues could be diminishing. Mine decommissioning is a costly exercise involving the removal of plant and infrastructure, rehabilitating all remaining disturbed areas, and monitoring and maintaining the area for a period into the future (Tables 1 and 2, indicative costs adapted from EA, 2002). While progressive rehabilitation assists in keeping liabilities to a minimum, the nature of most operations dictates that much of the disturbed areas are active until the cessation of mining and processing.

While adequate financial provisioning by the company represents 'best practice', most governments now require financial sureties to be lodged for mining operations in order to protect the public's interests and minimize ongoing liabilities. Financial institutions may also seek to include mine decommissioning costs and potential ongoing liabilities for due diligence on project finance and under terms for guarantees on unconditional performance bonds.

Table 1
Indicative earthwork costs

Area	Activity	Unit Cost (2002 A$)
Hardstand areas	Profiling	\$400–500/ha
	Surface scraped (saline soils)	\$2,500–3,000/ha
	Minor ripping (no seed)	\$300–400/ha
	Hydrocarbon contaminated soil excavation	\$1,000–15,000/ha
Roads	Edges graded (minor unsealed roads)	\$50–80/km
	Surface scraped (major sealed or capped roads)	\$2,500–3,000/ha
Pits safety bund construction	Placement of rock bunds	\$15–30/linear m
Waste landforms and TSFs	Battering/contour/profiling work (highly variable depending on material and slope)	\$5,000–20,000/ha
	Rock armouring and drainage control structures (e.g., rock drains)	\$40,000–50,000/ha
	Oxide material placement and spreading (<0.5 m)	\$7,000–8,000/ha
Tailings storage facilities	Capping with 1 m material	\$25,000–40,000/ha
Leach pads	Reshaping and capping	\$20,000–40,000/ha
General rehabilitation	Topsoil spreading	\$2,000–3,000/ha
	Ripping and seeding	\$1,000–2,000/ha
	Manual seeding only	\$500–1,000/ha

Table 2
Infrastructure demolition and removal or disposal

Item Description	Cost/Unit[a] (2002, A$)
Primary crusher (per unit)	$40,000–60,000/unit
SAG mill (Semi-autogenenous grinding)	$50,000–80,000/unit
Ball mill	$40,000–60,000/unit
Tankage CIP/thickeners, etc.	$10–20/m^3
Conveyors	$30–50/linear m
Power poles/lines	$2,000–3,000/km
Poly pipe 100/400 mm	$2,000–3,000/km
Transportable units	$2,000–3,000/unit
Fuel storage tank	$5,000–30,000/tank
Elution circuit	$20,000–30,000/unit
Gold room	$20,000–30,000/unit
Water storage tanks	$2,000–5,000/tank
Cyclone mesh fence	$2–5/linear m
Light industrial buildings (includes concrete floor)	$60–80/m^2
Heavy industrial buildings (includes concrete floor)	$80–100/m^2
Concrete slabs and footings	$40–60/m^2

[a] Assumes materials and plants have no resale value – dismantle and dispose. (Tables 1 and 2, indicative costs are adapted from EA (2002) and have no basis to IAS 16, CICA 3110 or US FAS 143 Standards and codes. Costings are based on limited experience of author only, and should not be considered as anything more than a 2002 guide to costs).

In addition to direct cost estimates for earthworks, revegetation and fixed-plant decommissioning, a contingency for general cleaning up and removal of minor, unaccounted, infrastructure must also be included. An approach that is being applied to many closure cost estimations is to include a general contingency as a percentage of overall costs. The figure used depends on the nature of the disturbances as well as the uncertainty associated with estimating the extent of work required.

Provisions also need to be made to cover management and monitoring costs over and above normal salaries for key personnel during operations. This is largely to cover management personnel costs after operations cease as well as for any specialist staff and/or consultants required to supervise infrastructure removal or rehabilitation and monitoring. This contingency would also include initiatives such as relinquishment audits for closed areas.

Similar to general contingency provisions, the approach being adopted by a number of operations is to include management and monitoring provisions as a percentage of overall costs; figures used for management and monitoring typically range from 10% to 35% depending on a range of site-specific factors.

Early closure planning puts the company in a position to understand its potential costs early in the mine life. Financial provisioning can commence at the conceptual closure planning stage but may be highly inaccurate, as it is difficult to predict the course of mine development. However, the initial cost-estimate exercise helps a company to focus on the areas of decommissioning where there is the greatest uncertainty in the outcomes. This enables priorities to be set for further work and research studies to better define required outcomes and hence decide costs over the life of the operations (Environment Australia, 2002).

Many factors play a large part in reclamation planning and these include company environmental policy, society's expectations of industry, an understanding of the reclamation requirements and policies of the principal regulatory authorities, and the varied and diverse needs of other stakeholders. Although all these anthropocentric factors drive reclamation planning, ultimately the final land use at that time has to be the prime consideration for reclamation. In some cases, this may have values that are not purely confined to the immediate land use needs, but are those of the broader ecosystem in which the tailings remain stored (Lacy, 2002).

As with all reclamation processes, a staged programme is required to capture all decommissioning issues, a path similar to that developed and used by the author is suggested in Fig. 1 (adapted from Lacy and Campbell, 2000). Tailing reclamation is most effective if approached in a systematic way and requires a specific understanding of the physical, biological and chemical nature of the specific tailing and involves work by people of many disciplines (Lacy, 2002).

3. STAKEHOLDER ENGAGEMENT AND ACCEPTANCE OF PLANS

Stakeholder engagement stands out as one of the most fundamental principles for effective mine decommissioning. Stakeholders include individuals, government agencies, community groups or others who are affected by or have an interest in the mine closure.

Mining is generally a transient activity, which is often responsible for substantial changes in both the community and the environment in which it operates. Stakeholders' interests often precede the mining operation and remain long after mining ceases. These interests often relate to alternative ongoing land uses, retention of infrastructure for public use and the maintenance of sustainable non-mining-based communities. Under some circumstances, stakeholders' livelihoods may be directly or indirectly dependent on the mine. Mine closures can cause significant social concerns, particularly in

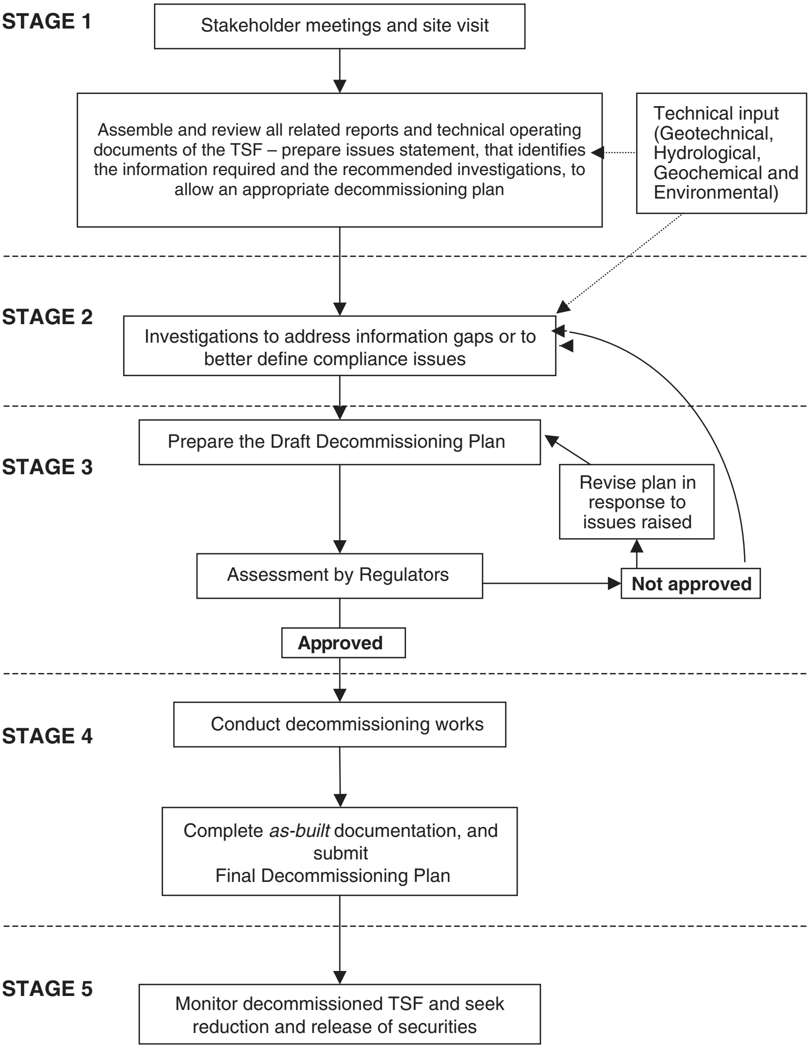

Fig. 1. Tailings (TSF) decommissioning flowsheet (adapted from Lacy and Campbell, 2000).

local communities where the mine may be the major commercial activity (WMI, 1994).

It is therefore essential that these interests be considered in all aspects of decommissioning planning and implementation. This is most effective when there is early involvement of key stakeholders in the operational planning and continuing liaison throughout the life of the project. Engaging stakeholders in meaningful dialogue is not just a matter of holding a public meeting to present the company's pre-determined decommissioning plan. It is a two-way exchange where all participants feel that their input is valued and will be given serious consideration in the process of developing and implementing the plan (Environment Australia, 2002).

Principles for stakeholder engagement in mine decommissioning can be defined as follows:

- *Identification* of stakeholders and interested parties is an important part of the mine closure process.
- *Effective consultation* is an inclusive process, encompasses all parties and should occur throughout the life of the mine.
- A *targeted communication strategy* should reflect the needs of stakeholder groups and interested parties.
- *Adequate resources* should be allocated to ensure the effectiveness of the consultation process.
- Wherever practical, *work with communities* to manage the potential impact of mine closure (ANZMEC/MCA, 2000).

Effective engagement with relevant stakeholders will assist in:

- developing realistic employee, community, and regulatory expectations;
- establishing a satisfactory post-closure land use;
- understanding internal and external stakeholder issues;
- enabling stakeholders to participate in the process;
- enabling stakeholders to prepare for closure;
- minimizing dependency on the company;
- avoiding costly surprises.

4. DECOMMISSION PLANNING, REHABILITATION, AND CLOSURE

There are no standard formulae that can be applied to determine decommissioning and closure outcomes, as all operations are unique in terms of potential long-term effects on the environment and communities. Appropriate mine decommissioning outcomes need to be determined on a site-specific basis taking into account the nature of the project in the context of regional factors such as climate, land capability, landform, water resources and ongoing land uses (Environment Australia, 2002). The author primarily discusses Australian experiences as that is where the author primarily operates and therefore there is a leaning towards challenges related to semi-arid and arid situations. Many principles remain generic, however.

The following factors are important when considering decommissioning options:

- public safety hazards and risks;
- ecological compatibility;
- potential as an ongoing source of pollution;
- community expectations;
- future land use and resource demands; and
- aesthetics.

In general terms, the basic environmental objectives of rehabilitation should be in accordance with the following criteria related to tailings disposal:

- Disposal of tailings should be non-polluting, both during operation and after de-commissioning.
- The tailings disposal structure should remain stable in the long term with regard to engineering aspects and erosion, and be maintenance-free.
- The final landform produced should be compatible with the surrounding landscape (Clark, 1987).

Tailings are often inhospitable to plant growth owing to their chemical and physical properties and the plant seeds encounter difficulties during the germination stage (Barth, 1988). There are many characteristics of tailings that render them difficult for plant growth. For instance, tailings contain low levels of essential plant nutrients (*e.g.* nitrogen, phosphorus) and are depauperate in terms of natural organic matter and associated microbial populations (Dean *et al*., 1986; Emerson *et al*., 1992). Tailings often contain high levels of salts (Petersen, 1992) and heavy metals that can act as phytotoxicants (Ritcey, 1989). The materials have poor physical composition and are often unconsolidated sands, which when mobilized by wind, sandblast and bury plants (Emerson *et al*., 1992). There is either intense reflection or absorption of solar radiation on the tailings surface, causing physiological stress to plants (Emerson *et al*., 1992).

Pickersgill (1994) suggested that for a medium (such as mine tailings) to be fertile for plant growth, it must have:

- desirable physical properties (*e.g.* adequate aeration and water-holding capacity, and low resistance to root penetration);
- an adequate supply of essential macronutrients (nitrogen, phosphorous, potassium, calcium, magnesium and sulfur) and micronutrients (copper, zinc, iron, manganese, boron, molybdenum, cobalt and chlorine);
- low concentrations of phytotoxic elements; and
- beneficial microbes without the presence of pathogenic species.

The history of the TSFs is critical to decommissioning; good records of use and construction can significantly influence the success or failure of the final decommissioning. There are a number of difficulties that may arise during the decommissioning and rehabilitation of a TSF, which are discussed below.

4.1. Principal properties and difficulties

Resource constraints and cost constraints may also impose difficulties during decommissioning. With these things in mind, there are a number of environmental factors that often influence the long-term stability of TSFs. A list of potential difficulties is given below.

4.2. Erosion

Tailings are often skeletal, fine and dry. Strong winds blowing across the flat upper surfaces of a TSF may cause saltation, detachment of soil particles, and subsequent dust generation. The unconsolidated and unprotected soils are open to significant water erosion, particularly in areas of regularly or episodically high rainfall. To minimize erosion, the walls of the TSF should be built using sound-stable materials, preferably with wall slopes of 20° or less, and if constructed of tailings covered as soon as practicable. Cover materials with high percentages of easily dried fines should be avoided. Fine rocky aggregates will provide more sustained protection. Ensuring that there is adequate vegetation on the facility walls after construction will assist with stability against erosion; however, if the facility is in use, deep-rooted species, whose roots may seek water, may affect wall integrity. Walls constructed of tailings are most at risk of erosion, and wherever possible it is advisable to avoid their use and cover these walls with waste rock prior to revegetating.

4.3. Water management

Many factors are involved in tailing-facility hydrology, in particular, evaporation. Evaporation partially dictates the amount of water contained within a facility, and consequently, the survival of vegetation is affected if water is not available for plant growth in the upper surface material. The clay content, drainage and nature of deposition also affect hydrology within the facility. Salinity has a critical effect on evaporative processes. Saline crusts are found to considerably reduce evaporative effects (Fahey, 1994).

The nature of the tailings and the proposed rehabilitation strategy dictates whether water should be retained or redirected. Overtopping of walls on a water-retaining facility can result in severe uncontrolled erosion and potential dispersion of tails to the environment. Water-shedding structures, on the other hand, have to be soundly designed at the civil engineering level, and potential pollutants that may be water-dispersed have to be evaluated.

Leaching of toxic material or salts into ground water may occur in some facilities and can impose a risk to other users of the ground water. Appropriate water-balance information may be used to model such potential problems. If the TSF contains potentially acid- or toxicant-generating material, then it may be necessary to redirect water off the facility, rather than risk long-term groundwater contamination. If the tailing is considered relatively benign, then water may be contained within the facility, thereby boosting revegetation in the long term. It is imperative that water management be considered during the earthworks phase of decommissioning.

4.4. Options in closure and rehabilitation strategies

The author suggests that there are a number of options for tailing rehabilitation, and the treatment(s) employed is largely dependent on the nature of the TSF. This implies that final decommissioning choices will depend on the challenges related to that particular TSF. Initial evaluation should give clues as to the strategy that should be trialled, or if confident, applied on a broad scale. According to Lacy and Ward (1998), the following options are available for rehabilitation.

4.4.1. Physical stabilization

This is the application of a physical mulch layer or barrier to the tailing materials to counter erosive effects of wind, water, and other disturbances. The advantages are its resilience and stability over time and therefore its protection of the local ecosystem. It can also be conducive to plant colonization and provide a niche for seedling establishment, through provision of inherent stability, favourable microclimate and protective nature.

There are often various cover mulches available. Readily available mulches include: oxide waste rock, laterite waste rock, topsoil, competent rock (non-acid forming), mill scats, alluvial mining gravels, underground, development waste, glacial till, and potentially spent heap-leach materials. Other forms of mulches that may be available include: vermiculite, smelter slag, fly ash, organic mulch products (sewerage sludges, straw, bark, compost, wood chips, forest products, and organic green wastes from towns and cities). Physical barriers (windbreaks) such as fences or artificial barriers may also be used, in an effort to achieve initial stabilization.

4.4.2. Vegetative stabilization

This is the establishment of vegetation to create the same effects as a physical barrier, while returning the storage area to a beneficial use by the organisms of the local ecosystem. The vegetation may also improve the qualities of the tailings by biological and physical processes, and at the same time improve the aesthetics of the rehabilitated facility. Concentration of toxic elements and metals within the vegetation may occur, so final use of the facility, or even the environmental risk of using vegetation as part of a cover combination may have to be carefully considered.

4.4.3. Chemical amendments

There are a variety of chemical amendments available, for example, gypsum, polyvinyl alcohol, lime or limestone and fertilizers. These ameliorants alter the physical structure or chemical make-up of the tailings to make them conducive to the establishment and survival of plants.

4.4.4. Chemical stabilization

These are artificial alterations of the tailing surfaces and are used in circumstances where the surfaces are very unstable. The sealants are sprayed or incorporated into the surface of the tailing to create a hard or non-erosive crust, designed to prevent wind and water erosion. Examples of chemical stabilizers include: resinous adhesives, bitumen-based compounds, sodium-silicate chemicals (geopolymers), lignosulfonates, cement, and elastomeric polymers.

4.4.5. Combinations

It is not unusual to use a combination of these different options during rehabilitation. Hydromulch seeding is an example of stabilizing processes using a combination of physical, chemical and vegetative stabilization. To achieve successful rehabilitation in the end, it is likely that combinations of treatments would be the best option. This would ensure not only increased stability, but also enhanced aesthetics.

4.5. Variability

Tailings are site-specific – there can be a high degree of variability between and within different TSFs. Differences can be created by ore types and geochemistry, the process used for ore extraction, the process water quality, the disposal technique and the environment in which the TSF is situated (Lacy, 2002). To date, many researchers have found that individual TSFs are unique structures and their geotechnical, physical and chemical properties may vary significantly from site to site. Expertise is therefore most likely required in the areas of geotechnical engineering, hydrology, geochemistry and rehabilitation, for adequate closure planning (Fig. 1).

In addition to the effects created by climate, surrounding land use and topography, tailing residue sites can have discretely different material characteristics associated with the mineralization and metallurgical processing. In fact, the cells within a tailing storage can show considerable variation (Morris, 1992). To create a medium suitable for revegetation, environmental practitioners often attempt to amend inhospitable tailings. While attempting to revegetate gold tailings in South Africa, Chenik (1963; cited in Barth, 1988) found that most amendments to the tailings were unsuccessful, but placement of soil in potholes, constructed on the tailings, did establish grasses. Effectively this process is the application and use of a soil cover. Even if protective soil layers and rock mulches are placed over tailings for stabilization, erosion can still occur. Vogel (1981; cited in Barth, 1988) found that the most effective method of erosion control was the establishment of vegetation, but Morris (1992) suggests that vegetation covers alone are often not sustainable in the longer term. The present author suggests that in general, a combination of soil or rock covers in association with vegetation might offer the most protection and stability to the often highly erosive tails material (Lacy, 2002; Lacy *et al.*, 2004).

The decommissioning process must cover all aspects of the operations in a site-specific manner. Table 3 outlines some suggested (but far from all) issues and consequences associated with closure aspects of a tailing decommissioning project. A risk analysis that investigates all the potential issues, consequences and possibly using options and techniques for managing these closure issues can be most informative. This approach is of considerable benefit in prioritizing and weighing up closure options prior to selection of a decommissioning strategy.

5. POST-CLOSURE MANAGEMENT, MONITORING AND RELINQUISHMENT

Unplanned closures are not cost effective and often result in substandard rehabilitation outcomes, as these works are remedial rather than integrated with mine planning. Substandard, unmanaged mine closures continue to damage the mining industry's reputation. The decommissioned mine determines what we leave behind as a legacy for future generations. If decommissioning and closure is not undertaken in a planned and effective manner, the mine may remain hazardous and a potential source of pollution for many years to come.

On the other hand, a properly decommissioned project, a site that remains safe and stable, is less likely to attract negative comment and to become a social legacy.

Relinquishment may be a staged process as progressive completion criteria and/or benchmarks are achieved. A sufficient period should have elapsed to demonstrate the stability of the site. For revegetated areas, this may require verification that the vegetation has reached, or is trending towards, a self-sustaining status. Potential impacts on groundwater may also take

Table 3
Closure of tailings storage facilities – likely issues

Issues and Consequences	Options and Techniques to Address Issues
Erosion and structural instability	
Overtopping from floodwaters	Geotechnical review/risk assessment on closure
High phreatic (water table) surfaces	Integrity from construction phase
Piping of materials during seepage	High-quality operational management
Sedimentation	Rock armouring
Surface flooding causing erosion of batters	Buttressing
	Drainage control
	Erosion resistant cover
	Surface hydrology and erosion protection
Acid rock drainage	
Internal and external instability	Geochemical characterization and selective discharge
Water-pollution impacts	Cover and capping research studies and design to reduce water and oxygen reactions
Acid soil	Identification of cover material source and availability
Toxic to biotic systems	Monitoring of cover performance and integrity
Gas and thermal emissions	Capture and release cover systems
Cover deterioration and failure	Use as backfill in open pits or underground operations
	Neutralization (*e.g.* lime) and treatment (antibacterial agents, and/or enhancing sulfide-reducing bacteria)
	Segregation/isolation/encapsulation
	Passive leachate management and treatment
Dust	
Visual impact	Surface capping to prevent wind erosion (*e.g.*, rough cover, rock mulching)
Offsite pollution effects	Wet cover/wetlands
Faunal impacts (over-grazing or digging)	Revegetation
	Wind breaks
	Hydromulch
	Fencing, isolation, management
Groundwater	
Aquifer contamination	Reduce hydraulic head by water shedding
Limitation of beneficial use	Integrate capture release systems
Recharge impact	Utilize evapotranspiration
Localized mounding	Cap and cover with capillary break
	Drainage diversions
	Groundwater recovery

Table 3 (*continued*)

Issues and Consequences	Options and Techniques to Address Issues
	Neutralization and detoxification of tails seepage
	Wetland filtration
Aesthetics	
High visual impact	Revegetated
Industry reputation	Effective landform and cover design
Negative public reaction	Stakeholder engagement
Public and fauna safety	
Injury or death	Effective landform and cover design
Toxicity (water and vegetation)	Restricted access
	Metal uptake and availability studies
Long-term viability of rehabilitation	Effective long-term land use planning
	Stock and feral animal control and effective monitoring

Adapted from EA 2002.

several years of monitoring to establish or refute this (Environment Australia, 2002).

After the decommissioning works have been undertaken, whether progressive or final, the main focus of the closure plan is monitoring and maintenance. The monitoring programme should be designed to demonstrate that the completion criteria have been met. This period should also plan for remedial action where monitoring demonstrates that completion criteria are unlikely to be met. If progressive rehabilitation has been successful, with stabilization and revegetation meeting completion criteria, then this last phase of closure may be shortened (ANZMEC/MCA, 2000).

The post-decommissioning monitoring programme should be similar to monitoring undertaken during the progressive rehabilitation but scaled back to focus on those aspects of the site that either relate to a potential ongoing pollution hazard or provide an indicator for how well the rehabilitation is progressing. An indicative post-decommissioning sampling and monitoring programme is provided in Table 4.

The objective of all decommissioning operations is to reach a point where the company has met agreed completion criteria to the satisfaction of the responsible authority.

Relinquishment effectively occurs at the point in time when the company has achieved all agreed standards and completion criteria for mine decommissioning. It is therefore very important that completion criteria are clearly defined. All parties should be satisfied that the site is no longer a danger to public health and safety, is not a source of ongoing pollution or

Table 4
Indicative post-decommissioning monitoring programme

Issues and Consequences	Options and Techniques to Address
Tailings storage facility	
Stability	Geotechnical survey and inspection
Seepage	Monitoring bores – quality
Erosion	Visual, photographic, sediment loading in runoff, EFA
Vegetation establishment	Transects to measure, density, cover, diversity, EFA, photographic, general regeneration
Dust	Deposition dust gauges, high volume samplers
Water quality	Standards, stream sampling, surface water testing

EFA – Ecosystem Function Analysis (Tongway, 1999).

instability and allows a productive use of the land similar to its original use or an acceptable alternative. In some instances, such as where land has previously been used for agriculture, the mining company should aim to relinquish land that is in a better condition, environmentally, than it was prior to the commencement of mining (Environment Australia, 2002).

It is important that an accountable authority is identified and held to make the final decision on accepting closure. The responsible authority will make a judgement on the achievement of the agreed completion criteria after consultation with other involved regulatory agencies, including the future land manager (ANZMEC/MCA, 2000). This applies to both financial securities and tenure over the mining area.

The site should not endanger public health and safety, should alleviate or eliminate environmental damage, and allow a productive use of the land similar to its original use or an acceptable alternative. A site requiring active maintenance is unlikely to be acceptable to government agencies. Release of securities and bonds may be progressive and reflect the progress of rehabilitation. Records of the history of a closed site should be preserved to facilitate future land use planning (ANZMEC/MCA, 2000).

Under some circumstances the company may be required to retain some ongoing liability under broad environmental or civil laws for specific aspects of the operation for an indefinite period of time.

6. CONCLUSIONS

Environmental impacts of tailings must continue to be reduced by the industry. The maintenance of ecosystems surrounding a mine site is a primary responsibility of the human beneficiaries of that industrial activity. Thus, the stabilization of tailings storages is of primary consideration during the operation and at the conclusion or temporary suspension of the mining operation. The author suggests that in many cases it is the failure, or lack of attempt to effectively rehabilitate tailings facilities, which presents itself as the primary reason for the communities' ingrained distaste of the minerals industry. Failure of facilities to retain the contents during operations and on closure and the resultant pollution from those incidents is often the cause of community outrage.

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PART II UNIT OPERATIONS

II.1 *Comminution*

Developments in Mineral Processing, Vol. 15
Mike D. Adams (Editor)

Chapter 12

Comminution circuits for gold ore processing

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1. INTRODUCTION

For the vast majority of ounces of gold produced, comminution costs in the form of power, grinding media, and liners represent the single largest cost category of milling. Heap leach operations, of course, have a substantially lower milling unit cost. The top 20 producers of gold in 2003 (see Table 1) accounted for approximately 30% of the world's total production of 83.4 million ounces. Within the 20 largest operations, over 90% of the ounces were produced by milling operations, and the majority of these ounces come from high aspect ratio semi-autogenous grinding (SAG) mill circuits, with significant contributions from low aspect ratio SAG mills, particularly in South Africa. The single largest gold producer in 2003 was PT Freeport Indonesia (PTFI), producing 3.3 million ounces. The PTFI mills treat ore from the Grasberg (open pit) and Deep Ore Zone (underground) deposits, and recover gold contained in copper concentrate via flotation and gravity circuits.

Since SAG ball-mill circuits represent the single largest type of gold milling comminution circuits, such circuits will be the focus of this chapter. Much has been written about SAG milling, and readers are referred to the volumes of the three SAG conferences (conducted in Vancouver in 1989, 1996, and 2001; University of British Columbia, Vancouver, Canada) for an in-depth discussion of various topics. A broad overview of various grinding circuits is presented by Callow and Moon (2002). Rather than review the existing state of

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Table 1
Top gold producers, 2003

Mill Complex	2003 Production[a] (Million Ounces)
Grasberg	3.3
Yanacocha	2.9
Newmont N. Nevada Op'ns	2.5
Barrick Goldstrike	2.1
Muruntau	1.8
Driefontein	1.2
Kloof	1.1
Cortez	1.1
Sadiola	1.0
Pierina	0.9
KCGM	0.9
Porgera	0.9
Great Noligwa	0.8
Morila	0.8
Kumtor	0.7
Geita	0.7
Beatrix	0.7
Tau Tona	0.6
Masimong	0.6
Batu Hijau	0.6

[a] All production data were collected from the operating company's annual report, except Muruntau's, which is estimated.

the art or make an attempt to condense the large body of existing literature, this chapter will focus on contemporary issues and trends in large SAG circuits, and on comminution topics typically of interest for gold operations.

2. CIRCUIT DESIGN ISSUES

Most aspects of SAG mill circuit design are well covered in the literature; however, the unit power requirement for SAG milling (both individually and as a fraction of the total circuit power) is worthy of additional discussion. Unlike ball-mill circuits, it can be very difficult operationally to trade grind for throughput in a SAG circuit. Once designed and constructed for a given ore type, a SAG mill circuit has only limited flexibility to deliver varying product sizes. This is particularly true for those SAG circuits designed with a coarse closing size. As a result, undersizing a SAG mill has disastrous results on throughput, while oversizing a SAG circuit results in a poor utilization of capital.

Traditionally, many engineers have approached SAG circuit design as a division of the total power between the SAG circuit and ball-mill circuit, often at an arbitrary power split. While this approach may result in a successful design, it ignores the critical decision of determining the correct power split between the SAG and ball-mill circuits. An illustration of the extremes in SAG circuit design is gained by comparing single-stage autogenous milling in a circuit closed with cyclones to a high ball-charge SAG circuit closed with screens. In many cases, the selected circuit configuration can be used as a guide to tailor the power input required for the application. Because the design of SAG mills often control circuit throughput, it is essential to install sufficient SAG power for the ore's unit power requirement. Rather than design the SAG circuit with an arbitrary fraction of total circuit power, it is more useful to base the required SAG mill size on the product of the unit power requirement for the ore and the desired throughput, and then size the ball mills based on the required finish grinding. Once operational, the selected SAG mill size and operating conditions primarily control circuit throughput, while the ball-mill circuit installed power controls the final grind size.

Particularly at mines where ore has become more competent during the life of the mine (and ore rarely gets softer as the mines go deeper) or at operations where the SAG mill was undersized during design, operators find themselves limited by a SAG mill's throughput capacity. The SAG operator who has not been asked to 'find a way' to 'push ore' through the SAG mill is rare indeed! As a result, many (if not most) operators view the SAG mill as a restriction in the grinding circuit that must be overcome, instead of a comminution unit operation required to prepare ball-mill feed.

Clearly, a SAG circuit design that has sufficient capacity and flexibility to attain design throughputs with the projected material types is essential. There are a number of small-scale tests in wide use that are designed to determine breakage characteristics and facilitate circuit design. All the tests balance compromises between the sample size required (in terms of both mass and top size), the modes of breakage evaluated, the utility of the test data for various design methods, ability to interpret the effect of steady-state conditions, as well as test complexity and convenience. Traditionally, the benchmark for determining the unit power required is pilot-scale testing; however, even pilot testing is limited by mill configuration and scale effects, and constrained by sample availability (Mosher and Bigg, 2001). The 450-mm SAG mill test (a fully continuous, steady-state test) offers a convenient small-scale methodology to evaluate the unit power requirements for SAG milling. The unit power requirement, in addition to the (semi-) autogenous work index calculated from the test data, provides useful data for SAG circuit design. Fig. 1 compares the distribution of unit power requirements for small- and pilot-scale data (McKen, 2004).

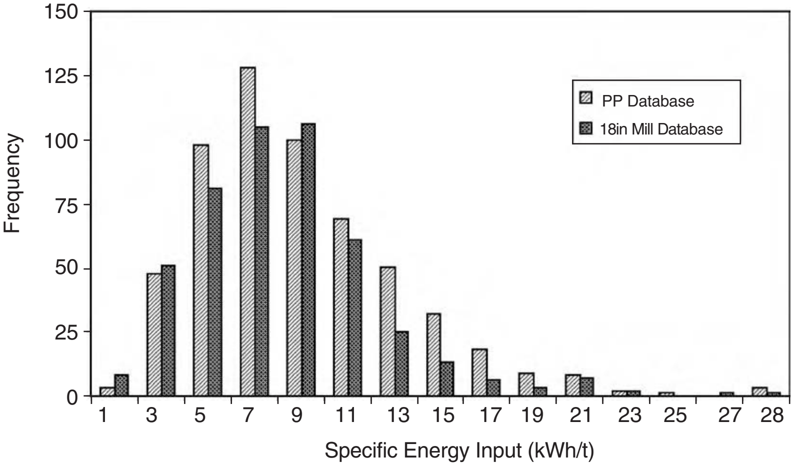

Fig. 1. Distribution of specific energy requirements for 450 mm (18″) bench-scale SAG and pilot-scale unit power requirements.

Despite the differences in scale between the 450 mm test and the 1.8 m pilot plant tests (along with differing circuit closing sizes, and varying pilot-plant operating conditions), the similarity in distributions of unit power requirements reinforces the concept that SAG throughput is defined by a specific unit power requirement.

3. DRILLING AND BLASTING

Improved fragmentation due to either more aggressive or more effective drilling and blasting operations can improve downstream comminution performance. At PTFI and other minesites around the world, operators have seen that the benefits of increased fragmentation in blasting extend beyond increased mill throughput. Improved fragmentation can also lead to higher shovel and haul truck productivity, reduced boulder handling/secondary blasting costs, and higher primary-crusher utilization. As the first step in comminution, drilling and blasting should be viewed holistically with the rest of the process. The obvious focus area is to minimize the overall cost of drilling, blasting, crushing, and grinding. The best approach, however, is not total comminution cost minimization, but overall revenue maximization. In evaluating the drill and blasting/comminution process, this implies that inclusion of recovery models is required to evaluate the true optimum.

Of course, it is important to keep in mind that more blasting is not always better. High fines generation can lead to excessive dust losses, and a lack of coarse, top-size material can limit grinding efficiency in autogenous or nearly autogenous circuits. As with most other processes, there is a point of diminishing returns for increased drilling and blasting effort.

Typically, blasting imparts roughly three times the unit energy of primary crushing. Efforts to improve blast fragmentation should include evaluations of pattern geometry, drill-hole size and spacing, stemming material, blast size (with larger blasts generally minimizing edge effects), powder factor, explosive type, and detonation timing. Of course, execution of the appropriate design is required for the best results. Having a blast design tailored for categories of material types and rock joint geometries will result in improved drill and blast performance while allocating assets to those materials that require them most; in many cases, additional costs for improved fragmentation in some areas can be balanced by cost savings in others. Finally, a feedback system for monitoring blast performance and improving future blast designs is required to close the loop. Fig. 2 presents the results of fragmentation characterization (by image analyses) of blasts of a single material type at PTFI, and is typical of the response from increased blasting energies.

Numerous case studies now exist in the literature detailing the effect of finer blasting on subsequent milling process. However, in many operations, particularly those with multiple ore sources or types, discerning the effect of feed size on mill throughput can be problematic. PTFI mills, for example, open-pit ore classified into five material types along with underground ore with two material types in four different concentrators. On a given day, open-pit ore comes from multiple shovels and is fed to one of three primary crushers. Underground ore from a block cave operation with a large number of draw points is also blended to selected mills. While the number of ore sources and mills at PTFI complicates destination tracking of discrete blocks of ore beyond that of most operations, separating the effect of material type and feed size on throughput is always challenging. Well-planned, rigorous, and well-executed campaigns are the best way to evaluate the effect of feed

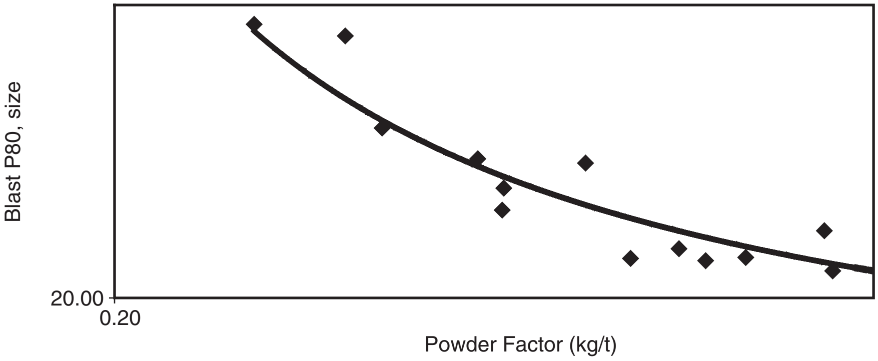

Fig. 2. Effect of increasing powder factor on blast fragmentation.

size on throughput. The complexity and operational disruption of such campaigns, however, make these campaigns difficult to be accomplished. Nonetheless, trends can be mined from plant data. Fig. 3 presents plant-wide data from PTFI's four concentrators that demonstrate close correlation between material type and plant throughput. PTFI's ores fall into three 'bins' for throughput modelling – hard, medium, and soft.

Notwithstanding the correlation of material type to plant throughput as observed in Fig. 3, feed size is an important variable for mill throughput. Each ore type tends to have a separate size-throughput response, but not all ore types are strongly sensitive to feed size. In fact, for substantial portions of PTFI's operating history, circuit throughput was not particularly sensitive to feed size (Partanen *et al.*, 2001). This was a result of ore breakage characteristics (relatively soft ore), the fineness of the mill feed (again as a result of feed characteristics, but also as a result of the ore-pass system), and the high-ball charges employed in SAG mills. A lack of sensitivity to feed size in mill throughput is also typical of operations that restrict throughput to attain a target grind size, that have limited ball-mill capacity, or other downstream constraints.

Despite a lack of sensitivity to feed size with softer ore types at PTFI, a significant correlation is seen with harder ores and blends. Fig. 4 presents the relationship between feed size and SAG mill throughput for one of PTFI's concentrators during a 3-week period when a variable ore blend averaging 40% hard material was milled. Correlations are stronger when milling a consistent blend, or when milling a single ore type. This data set was selected

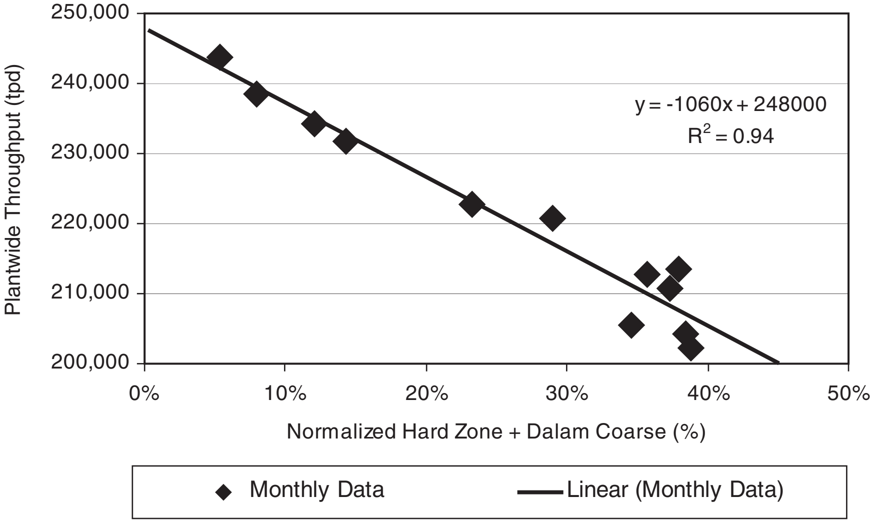

Fig. 3. Example of the effect of material type on mill throughput.

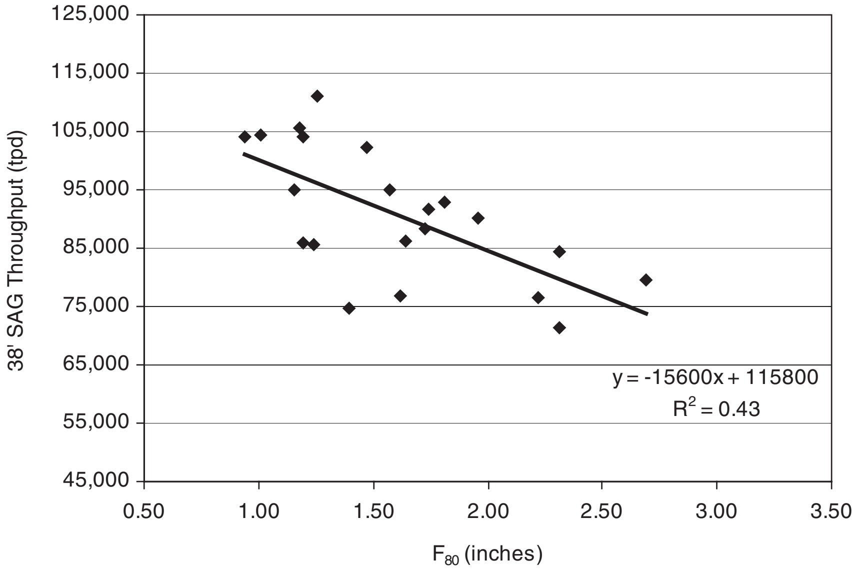

Fig. 4. Example of feed size on mill throughput for a blended ore.

to show both the relationship of feed size to throughput, as well as how varying ore blends can present challenges in masking the effects of material type and feed size. Some operations find improved correlations by looking at the top size, various passing sizes, or *fines* (often defined as material that is below grate size).

4. PRIMARY CRUSHING AND STOCKPILE MANAGEMENT

Reflecting the importance of primary-crushing performance on the milling process, many operations have transferred primary crushers from the operational control of the mine to the mill. Regardless of who operates the equipment, primary crushing has two customers: serving the mine to maximize load and haul equipment utilization, and also serving the mill to maximize overall comminution efficiency. Many mines select primary crushers based on top size of the designed or anticipated run-of-mine (ROM) ore. This can result in a substantial excess of primary-crushing capacity for smaller operations.

Frequently for large operations, though, primary-crushing capacity becomes an issue not only for milling operation (in terms of capacity and unit power input), but also for mine productivity. As primary crushing becomes taxed, issues that are conventionally dealt with in secondary, tertiary, or pebble-crushing roles become more critical. Management of gap setting, power draw, predicting and extending liner life within a specified performance envelope and productivity issues all become important to the overall comminution process. As with other crushing operations, employing stockpiles (or ore pockets), reclaim, or bins can maximize equipment productivity and efficiency. Most large gyratory installations are designed to accept direct dumping. While this minimizes the capital of the primary-crusher installation, it is inevitable that there is a trade-off with reduced primary-crusher utilization and crusher efficiency. This is a result of feeding the primary crushers based on the frequency that haul trucks present themselves to the crusher, instead of based on optimum crusher operation.

Management of the mill stockpile is critical to maintaining consistent throughput. Most operations reclaim from a stockpile of primary-crushed material. There is generally some degree of stockpile segregation, with coarse material preferentially accumulating towards the outside of stockpiles. Maintaining a live stockpile and balancing multiple reclaim feeders result in the highest average (and most stable) throughput. Maintaining the stockpile at reasonable levels minimizes the effect of load and haul equipment shift changes on downstream operations. The size of the stockpile should be based on anticipated fluctuations in production of primary-crushed material as a result of primary-crusher maintenance, load and haul asset maintenance, mill maintenance downtime requirements, and normal fluctuations due to mine planning and sequencing. Natural stockpile segregation can also offer opportunities to improve overall circuit operation, either via balancing the SAG mill and ball-mill circuits, or in cases, by preferential milling of ore from different feeders.

5. SAG MILL CONFIGURATION AND OPERATION

Over the past few years, there have been a number of focus areas in optimizing SAG mill operations. A major evolution in mill-shell lifter design has occurred, and much work has been done in the area of pulp lifters and slurry discharge. Progressively, more computationally demanding models (among them discrete element analysis and computational fluid dynamics) have been developed to complement more traditional, mathematically fitted, and population-balance models (Herbst and Nordell, 2002). These advanced techniques may offer the ultimate end state in mill modelling: the ability to integrate models of charge movement and energy spectra, particle breakage, slurry flow, and material wear. For now, while these advanced techniques help to shed light on the challenges of understanding and predicting mill performance, both shell- and pulp-lifter designs remain an experimental science. Some consensus, however, has emerged from the massive plant trial effort that has occurred over the past several years.

5.1. Lifter development

Shell-lifter design embodies many interrelated facets of mill operation: overall life (dictating scheduled downtime), charge trajectory (effecting both performance and liner protection), and the change in performance over the life of a liner. Several developments in SAG mill operation combined to make lifter face-angle a focus area: mills grew rapidly to 11.6 and 12.2 m (38 and 40 ft) diameters, mills were equipped with variable speed drives (typically allowing speeds up to 81–82% of critical), and the 'standard' ball size grew from 105 to 127 mm (with sizes of up to 152 mm trialled or used).

As mills and media size grew, and mills were operated at relatively faster speeds, the potential for liner damage increased. Work by many researchers indicates that the face angle was less critical with smaller mills, from both a performance and liner damage standpoint (Royston, 2003). At the same time larger mills were being commissioned with traditional shell lifters having little relief from vertical (with face angles of 7–12° being typical), a number of methodologies to predict charge trajectory and charge position were developed and implemented. The combination of newly available modelling technologies and the number of larger mills in service converged so that many operations trialled shell-lifter configurations with greater spacing (expressed in terms of the ratio of distance between lifters to lifter height), and/or with increased face relief.

Most operators reported that the more relaxed lifter face angle and wider spacing improved mill performance. There is little consensus, however, on whether improved performance was due to reduced lifter packing at start-up with new lifters, or due to improved process performance in terms of steel impacting the toe of the charge. After starting with 12° lifters, PTFI installed 18° then 25° lifters. Little or no throughput benefit as a result of the face-angle change was observed, but the relaxed angle decreased lifter packing, and therefore increased the total tonnage over the life of a liner set (Coleman *et al.*, 2002). At other operations, face angles of up to 35° have been tested; most operators report a loss of lifter life at angles greater than 25°. In terms of performance, improved performance has been claimed at face relief angles greater than 25°, while others have cited worse mill performance (Hart *et al.*, 2001; Banini *et al.*, 2004).

Much of the benefit of relaxed face-angle appears to stem from a reduction in lifter packing. Packed lifters are depicted in Fig. 5; throughput can drop drastically with packing of new lifters, due either to a lack of charge lift, the obvious reduction in mill volume, or a combination of both.

An analysis of published lifter trials and PTFI's experience allows drawing of some general conclusions concerning lifter spacing-to-height ratios. Lifters starting with a new spacing-to-height ratio of less than 1.5:1 are most prone to packing, while those with a new ratio of 2.0:1 or more show substantially

Fig. 5. Packed shell lifters after liner change-out in a 10.4 m (34′) SAG mill.

less packing. While there are indications that liner life tends to be shorter for liners with a new ratio greater than 2.0:1, maintenance life cycle should not be the only consideration (Hart *et al.*, 2001; Karageorgos *et al.*, 2001; Sherman, 2001; Tew *et al.*, 2003; Raabe and Bigg, 1996; Meekel *et al.*, 1996).

The trade-off evaluation between higher operational productivity and increased maintenance downtime for lifter change-out can be readily conducted and evaluated, and it is often worth selecting and changing liners based on maintaining a performance envelope than on the basis of the more traditional metrics of liner life and scrap weight. As a guideline, mill throughput is maximized between ratios of 2.5:1 and 5.0:1. It is evident from calculations based on lifter profiles that some lifters (particularly those prone to packing at start-up) will wear to the point that they lose lift before attaining the 5.0:1 ratio. These guidelines are stated without reference to face angle; in general terms, and at equivalent spacing-to-height ratios, lifters with greater face-angle relief will have less packing problems but experience greater wear than those with a steeper face angle.

The options for lifter spacing are limited without redrilling a mill shell, and only limited changes can be made with lifter height before the reduction in lifter life decreases plant production capability. Of course, lifter spacing, height, and face angle must be considered along with the SAG speed and operating mill volume at a given operation. Shell-lifter design remains an area of research and plant trial effort.

5.2. Pulp discharge

As mills have increased in size, the effect of the SAG mill discharge end design on throughput and grinding efficiency has been given a great deal of attention. Particularly for large mills, the volumetric efficiency (or pumping) has great importance. There has been a substantial study concerning backflow in pulp lifters; backflow potentially reduces throughput and milling efficiency and increases pulp-lifter wear. Such backflow can easily be seen in the conventional 4-into-1 pulp lifters, with chambers one and four (in a bi-directional mill) wearing prematurely due to slurry backflow. This wear pattern is depicted in Fig. 6.

To minimize backflow, PTFI has progressively opened the discharge end of the pulp lifters in its 11.6-m (38′) SAG mill to reduce slurry constriction and to limit the potential for backflow. Initially, this was achieved by adding 100 mm of pulp-lifter depth to the top end of the pulps, resulting in a steeper angle of the discharge grates relative to the mill shell. This modification was successful in increasing the mill's ability to attain higher volumetric throughputs (Staples *et al.*, 2001). Since then, the inner portion of the discharge end has been opened again, resulting in a compound angle on the mill interior of the discharge end. The discharge end of PTFI's 11.6 m (38′) mill is depicted in Fig. 7; these modifications have allowed the mill to reach a peak volumetric capacity of 5000 m^3/h. Clearly, grate and pulp-lifter design is critical in moving this amount of slurry. This volume is handled with a grate open area of 13.1%. Despite these modifications, some evidence of pulp backflow persists, and PTFI has initiated discharge cone indexing. This practice has been successful at equalizing wear between the four chambers of the pulp lifters and extending the required maintenance interval.

In addition to work with conventional pulp lifters, curved pulp lifters have been demonstrated to improve discharge efficiency. They have been installed

Fig. 6. Pulp lifter wear demonstrating slurry backflow.

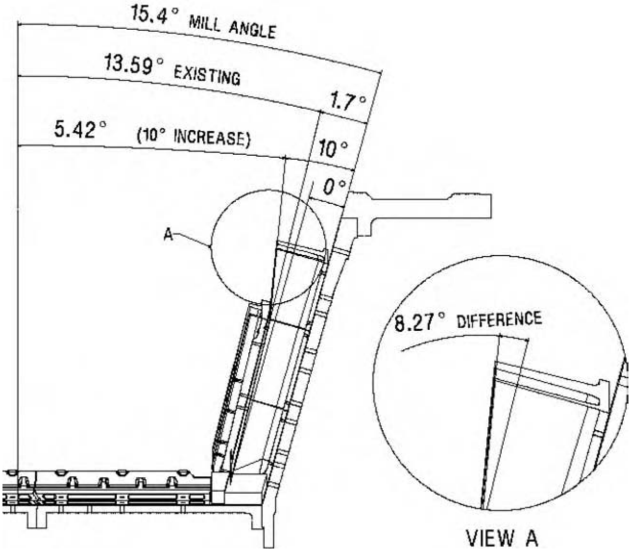

Fig. 7. Evolution of PTFI's 11.6 m (38′) mill pulp-lifter configuration.

at a limited number of operations, and have been observed to reduce wear. The major drawback of curved pulp lifters is the loss of the ability to operate a mill bi-directionally. While shell lifters can be designed to overcome this and retain all or most of the life with a bi-directional set, it often requires re-initiation of a liner development program.

5.3. Grinding media size

Several operations have experimented with progressively larger ball sizes in efforts to improve SAG throughput, particularly with hard, coarse ores. While the energy of individual impacts increases with larger balls, the number of impacts for a given load (or volume filling of ball charge) decreases. The optimum ball size for a given operation is a function of feed size, ore size, and competency, as well as mill operation conditions (speed, steel charge, and total mill volume). There is little consensus in this area. This may be a function of the difficulty in conducting and evaluating plant trials with ore of various feed characteristics (a relatively small performance benefit), or relate to the ore-specific nature of the optimum steel size. Alumbrera Mine reported trials of 140- and 152-mm-sized SAG steel compared to a 127-mm make-up ball, and indicated that 152 mm steel increased throughput for hard ore types, but offered no improvements for softer ores (Sherman, 2001). A trial conducted at PTFI showed that 127 mm steel was best for throughput, even for hard ore types; these data are presented in Fig. 8. In discussions of both the Alumbrera and PTFI data, *hard* and *soft* are strictly relative terms. No

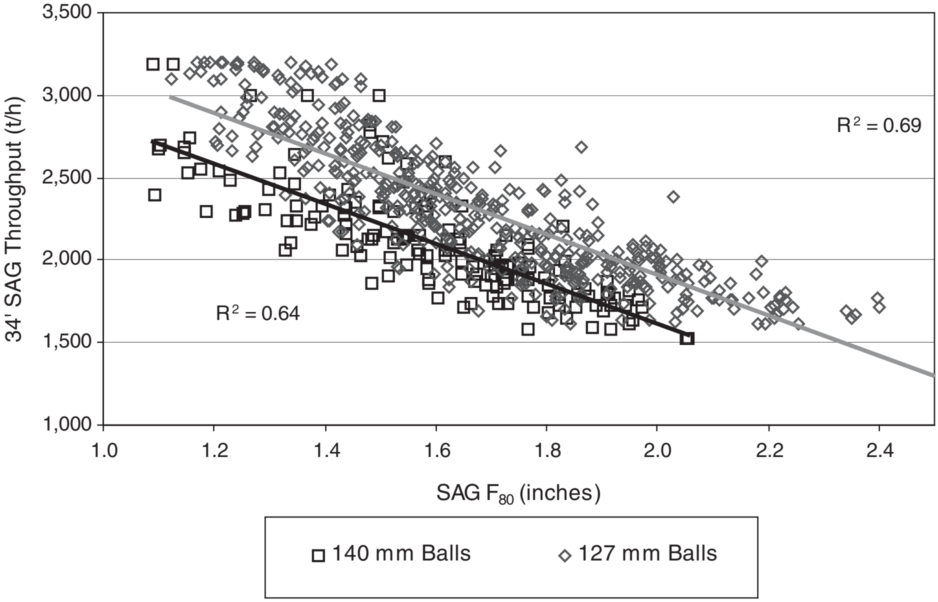

Fig. 8. Results of PTFI ball-size trials on SAG throughput.

analysis of the appropriate media size is complete without including a cost evaluation based on the steel cost, wear rate, and scrap size of each media under consideration.

5.4. Mill relines

No discussion of milling, and particularly SAG milling, would be complete without some mention of relining. Unlike a concentrator with multiple grinding lines, conducting SAG mill maintenance shuts down an entire concentrator, so there is rightly a tremendous focus on minimizing required maintenance time; reline time represents the majority of scheduled maintenance requirements.

Reline times are a function of the number of pieces to be changed, and the time required per piece. Advances in casting and development of progressively larger lining machines have allowed larger and larger liners. Like many operations, PTFI has devoted substantial resources to a liner development program to reduce the total number of liner pieces and fasteners. Vendor benchmarking has established that PTFI's 11.6-m (38′) SAG mill, for example, has nearly 40% fewer liner pieces than similar installed 11.6 m (38′) mills that have yet to complete liner development programs. While improvements in this area will continue, the physical size limit of the feed trunnion and the ability to manoeuvre parts will become an increasingly limiting factor. The other portion of the equation for reline times is time per piece, and performance in this area is a function of planning, training/skill level, and equipment.

5.5. SAG mill discharge classification

There are two primary mechanisms for classifying SAG mill discharge: screens and trommels. Due to a reduction in the required capital costs and space required for screens, trommels enjoyed a period of popularity, but the most favourable method of preparing SAG circuit oversize for pebble crushing is screening. All things being equal in terms of ore character and pulp density, screening produces a cleaner, drier oversize with much less fines carryover than does a trommel. This is particularly true for large SAG installations. As mill diameter increases, the volumetric throughput increases substantially faster than the effective screening area of a trommel. Trommel oversize like pebble-crusher feed has caused problems with pebble crushing at a number of operations. This is due to carryover of fines and moisture, which results in crusher chamber packing and ring bounce. Operations including Newmont's Batu Hijau have retrofitted SAG screens to supplement trommels, while Newcrest built and commissioned a circuit screening trommel oversize at Ridgeway after the trommel-only circuit at Cadia resulted in difficulties with the pebble-crushing circuit (Goulsbra *et al.*, 2003; Dunne *et al.*, 2001; Hart *et al.*, 2001). PTFI uses 3.0 by 7.3-m (12 by 24 ft) vibrating screens to classify SAG discharge, employing two on the 10.4-m (34 ft) SAG mill circuit, and three on the 11.6-m (38 ft) SAG circuit.

As most SAG circuits are now designed for the inclusion or subsequent addition of a pebble-crushing circuit, a design that incorporates screens allows maximum future flexibility. The method of returning the classified oversize to the mill requires mention. Some large SAG operations have been designed and built with water cannon return, including Kennecott Utah Copper and Alumbrera. With this system, the trommel oversize is returned directly to the mill with a water jet. Of course, the ability for these plants to retrofit pebble crushing into the circuits is significantly more complicated than if an external method of recycling oversize had been employed. It goes without saying that the oversize from the SAG mill classifier oversize must be returned to the mill via a belt system to use a pebble-crushing circuit.

The use of screens is not without complications. Attaining even feed distribution to multiple screens can be challenging, the maintenance requirements of screens requires that stand-by units (either installed stand-by, for use in a rotating spare program, or both) be used.

5.6. Pebble crushing

The first consideration when discussing pebble crushing is why there is a need for the unit operation. Secondly, the configuration of the overall pebble circuit merits discussion. Pebble crushing, almost a standard for SAG circuits today, was controversial early in the development of autogenous grinding (AG) SAG milling. This was largely due to the fear of failing to efficiently separate grinding steel from the recycle load, with subsequent crusher damage. Magnet and metal detector manufacturers have minimized this difficulty, and today, more SAG circuits are constructed with pebble-crushing circuits than without. Making an efficient steel–magnetite separation, however, remains problematic for some producers.

The need for pebble crushing stems from two factors: a depression in SAG grinding rates at certain particle sizes, and the accumulation of a harder fraction in the mill load. These factors typically result in a mill throughput increase with the installation of pebble crushing that is larger than would be expected purely on the basis of the additional power. Overall, pebble crushing can increase throughput as well as decreasing the total power required to grind to a given size. Typically, pebble crushing also coarsens ball-mill circuit feed, a consideration if a ball-mill circuit is already taxed.

The first case for pebble crushing, in order to compensate for decreased SAG grinding rates in the area between which impact or abrasion breakage dominates, deals with what is often referred to as the *critical size*. With the increase in simulation-based circuit modelling in recent years, more and more people have developed an understanding of the nature of the build-up of material in this size fraction, and the classic *s-shape* SAG breakage-rate curve is well known. The typical SAG breakage-rate curve (developed using the *JKSimMet* steady-state simulator package) is presented in Fig. 9, and demonstrates a depression in breakage rates in the 20–80 mm size fraction. When material in this size fraction represents a significant fraction of the mill load,

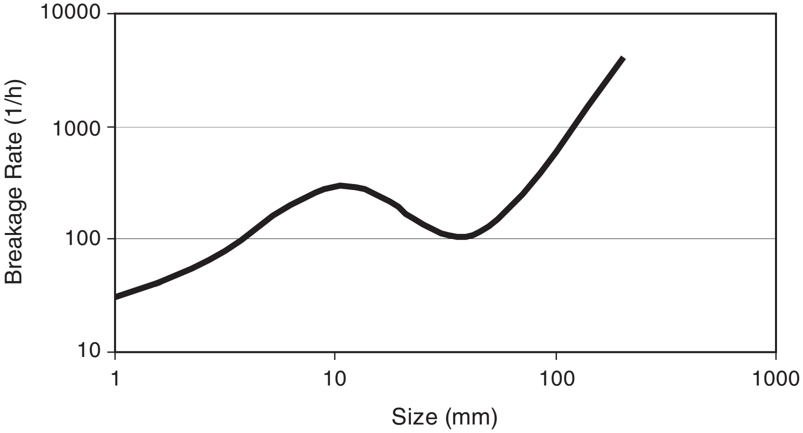

Fig. 9. SAG breakage rate curve.

SAG throughput can increase by as much as 50% of the total tonnage of pebbles crushed. Pebble crushing shifts the mode of breakage for these particles from fairly slow abrasion and attrition towards highly focused impact breakage.

The second type of build-up of critically sized material is based on having a combination of rock types in the feed that have different breakage properties. In this case, the harder fraction of the mill feed builds up in the mill load, again restricting throughput. Examples of materials in this category include diorites, chert, and andesite. When build-up of these materials does occur, pebble crushing can improve mill throughput even more dramatically than when the critically sized fraction results from size alone.

The definition of *critically sized* material is often misunderstood. Critical-size particles are those where the product of the mill feed-size distribution and the mill breakage rates result in a build-up of a size range of material in the mill load; this critical size can be of any dimension. That said, the concept of critical size has become almost synonymous with pebble-crusher feed, and therefore it is typically referenced as the size range of 13–75 mm. Such a definition ignores larger critical-size material that cannot pass the mill grates – such a size often results with very hard ore types that have received insufficient breakage in blasting and primary crushing. Throughput with these ores can benefit from improved blast fragmentation, primary crushing, or SAG pre-crushing. Without such feed-size reduction, however, additional pebble-crushing power may be of little benefit, because pebble generations can be quite low.

There are several critical design elements of a successful pebble-crushing circuit, including: material handling/diversion capabilities, metal removal, belt loading, pebble-crusher feeding, and return of crushed material to the circuit.

After classification, the SAG discharge oversize is conveyed to the pebble-crushing circuit. The conveyors should have provision for returning the oversize to SAG feed (during pebble-crusher maintenance, for example, or during periods when metal is detected). Additionally, the ability to reject oversize material can also be useful. This is useful for diverting material after metal detects (discussed below), for sampling, or in cases where metallurgical work confirms grade depletion, and allows rejection of the stream to waste. A travelling chute (as opposed to flop gates) to separate the stream between pebble-crusher feed and return to SAG feed offers the greatest flexibility.

The design of an efficient metal-removal system is critical. The risk of inefficient metal removal from the pebble-crusher feed is obvious, and allowing excessive mill balls to the pebble crusher will rapidly damage both crusher manganese and other crusher components. The present industry standard for metal removal is the cross-belt magnet. In design of cross-belt systems, sufficient belt capacity should be designed so that belts can be run with lower volumetric loading. In other words, at a fixed belt size and loading, metal separation is better with relatively faster belt speeds versus relatively higher belt loadings. Designing to a Conveyor Equipment Manufacturers Association (CEMA) belt loadings of 65% or less has worked well at PTFI, with peak loadings of up to 85%. PTFI has used belt speeds up to 3.8 m/s (750 fpm) successfully. As an alternative to cross-belt magnets, manufacturers have recently fielded magnets fitted to remove tramp metal from directly screening oversize as the oversize material is loaded onto belts. After the magnets for steel removal, metal detectors should be installed to detect any metal that bypassed the magnet(s). Such detectors should be upstream of a diverter gate, so that a metal detect results in diversion of the material back to the SAG feed.

For the most efficient operation of a pebble-crusher, provision for a surge bin should be included. The use of a surge bin to allow full-choke feeding improves crusher performance and helps ensure that crusher components wear more evenly. Far steadier operation (in terms of maintaining high power draw without power spiking) can be maintained with a surge bin than without. Perhaps the ultimate ‘surge bin’ is a pebble stockpile with reclaim feeders. In addition to the advantages of surge bins, the use of a stockpile of sufficient capacity can allow the benefit of not having to recycle pebbles back to SAG feed during periods of crusher maintenance, and can allow mill throughput to be maintained at high levels even if the pebble-crushing circuit capacity cannot keep up. The pebble accumulation can then be worked through during periods of increased SAG capacity (due to softer, finer ore, or other reasons). Obviously, the pebble stockpile must stay in balance. Asarco’s Mission Complex South Mill used a pebble stockpile; other operations have since followed this lead (Fisbeck, 2001).

The last major decision for a pebble-crushing circuit is where to put the pebble-crusher product. Conventionally, crusher product was returned to SAG feed. Some designs, however, now allow pebble-crusher product to be returned to the SAG screens/discharge (allowing operation of the pebble crusher in closed circuit) or even to the ball-mill circuit. There is no ‘right’ answer for where the crusher product should be put 100% of the time. Sending the pebble-crusher product to the SAG discharge allows the material to be classified prior to going to the ball-mill circuit, and relieves the SAG mill of loading. Sending the pebble-crusher product back to the SAG circuit allows for attaining a finer SAG circuit product, and can relieve the ball-mill circuit. Sending the pebble-crusher product directly to the ball-mill circuit can reduce SAG discharge screening requirements, but if pebble-crusher product size is not well controlled, ball-mill scatting problems could result. Given sufficient screen capacity, perhaps the best combination is to allow for directing the crusher product either back to the SAG feed, or to the SAG discharge screens. PTFI's C4 concentrator, with twin MP1000 pebble crushers, has the capability to send pebble-crusher product back to the SAG screens to allow crushing in closed circuit (and relieving the SAG mill), or to return crusher product to SAG feed (when the circuit is ball-mill limited). While the standard mode of operation is to return pebbles to the SAG screens for maximum throughput, the flexibility to return SAG feed is an excellent option to balance the SAG and ball-mill circuits during periods of ball-mill limitations. The circuit is depicted in Fig. 10.

6. BALL-MILL CIRCUIT OPERATION

Very often in SAG circuits, the ball-mill circuit is neglected. In many operations where economics dictate that throughput is worth more economically than the required sacrifice in grind, the focus shifts to throughput so much that the available ball-mill power is not used to the fullest extent. Even in those operations where a firm grind target is not adhered to and attainable throughput governs the balance of the circuit, it is foolish not to take full advantage of the installed grinding power. Ores for which recovery is grind insensitive in the range of the typical operation are unusual.

Given that mills are charged to the target ball charge with reasonably sized media, and the feed to the ball-mill circuit is not so coarse as to cause constant scatting, the key to efficient ball-mill circuit operation is efficient classifier operation. The standard classifier for ball-mill circuits is the hydrocyclone. Ensuring that the finest and most efficient cyclone cut involves selecting the appropriate cyclone configuration for the ranges of grinds that

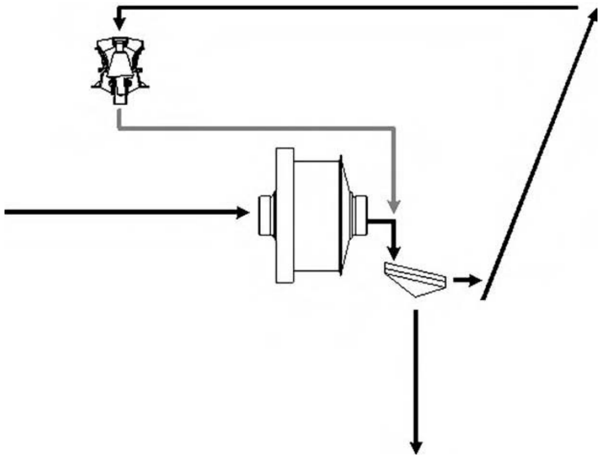

Fig. 10. PTFI's C4 pebble-crushing circuit.

will be encountered. The apex (spigot) size can be manipulated to deliver the maximum underflow density at the target operating conditions, with the vortex finder tailored for the desired product size. With a given configuration, adding the maximum amount of water (subject to cyclone feed-pump limitations, the minimum overflow density, and cyclone pressure) will generally result in attaining the finest possible grind. Employing a control system to maximize water addition to the cyclone feed pump (subject to pump capacities and downstream densities constraints) is often employed successfully to maximize ball-mill circuit grind.

There is strong evidence supporting the concept of using a mixed-size make-up ball to attain incremental grinding efficiencies in ball mills. There is little reason to believe that the steady-state media size distribution resulting from the wear rate of the make-up ball size corresponds to the optimum ball size based on the mills' feed and target grind. McIvor (1997), in his review of media sizing, points out that grinding efficiency improvements based on tailoring ball size to the application are well documented in Taggert's classic *Handbook of Mineral Dressing*. Later work has focussed more on mixed size make-up charging than solely on the top size. In general, a mixed make-up ball-charging regime improves grinding efficiency, with greatest benefits seen for single-stage milling applications with large size reductions.

Nonetheless, most operations tend to use a single-sized make-up ball for reasons of convenience. There is less conclusive evidence for the removal of fine steel from ball charges. While some operations claim an anecdotal benefit from removal of fine steel, unpublished studies by the author indicate a substantial benefit from the use of fine media (less than 12 mm) as a supplement to a conventionally sized make-up ball when grinding a gold ore to an 80% size of 75 µm. McIvor (1997) speculates that the only case where there is an advantage in removing fine media would be for very coarse grinds. It is possible that removal of ball chips, which may tend to float due to a shape factor and likely contribute very little to grinding, could result in an improvement in grinding efficiency.

7. GOLD RECOVERY IN COMMINUTION CIRCUITS

Hydrocyclones demonstrate a trait that is useful for gold mills – minerals with higher specific gravities having a progressively finer cut-size (whether this is desired or not). In plants with free-milling gold, this leads to gold concentrating in the milling circuits (see Fig. 11). On a size-by-size basis, concentrations of up to 100 times can occur in cyclone underflow. In this respect, hydrocyclones are outstanding rougher concentrators. Many operations take advantage of this effect by installing gravity-concentration units in

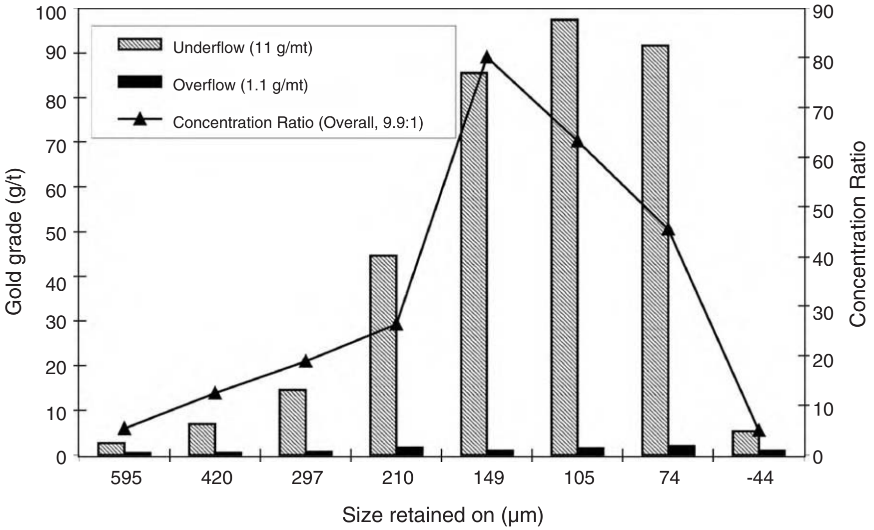

Fig. 11. Free gold concentration in an oxide gold mill ball-mill circuit.

the grinding circuit. Treating a split of the cyclone underflow is perhaps the most common, but ball-mill discharge and cyclone feed streams have also been treated. A discussion of the type of gravity device selected (conventional, high-G, jigs, *etc.*) is beyond the scope of this chapter, and is addressed in Chapter 13.

There are a number of considerations for gravity circuits fed by bleed streams. First is the effect on the overall circuit water balance. As the gravity tailing (which represents nearly 100% of the feed mass) is typically returned to the ball-mill discharge sump, any water addition in the gravity circuit will affect the grinding circuit's overall water balance. In most cases, the water balance can be adjusted with other streams in the ball-mill circuit, but the overall water balance should be carefully considered.

Most circuits treat cyclone underflow, but ball-mill discharge is also sometimes used as gravity-circuit feed. In either case, feed to the gravity circuit can be pre-concentrated to a certain extent. For cyclone underflow streams, weirs can be constructed in the underflow tubs. In this case, cyclone underflow is fed to a weired area in the underflow tub, and gravity-circuit feed taken from this area. Slurry excess to the capacity of the gravity circuit overflows back to ball-mill feed. For those circuits treating ball-mill discharge, a sluice can often be arranged to provide some pre-concentration for the gravity circuit.

Flash flotation is also used in comminution circuits for gold recovery, and is covered in detail in Chapter 14. The application on cyclone underflow is generally similar to integration of a gravity circuit. Flash flotation can be used solely, as at Louvicourt (Laplante, 2000), or gravity and flash flotation circuits can also be combined or integrated, as in Newcrest's Cadia Hill operation and the Telfer design (Goulsbra *et al.*, 2003).

Milling-in-cyanide is also conducted by many operations. Cyanide and lime are added to the grinding circuit, often with trimming of both pH and cyanide levels during the subsequent leach process. There is relatively little information published concerning leach kinetics, but the addition of cyanide to the milling circuit clearly initiates the leach process earlier. This practice is not recommended for those ores that contain *preg-robbers* (which necessitates the use of carbon-in-leach (CIL)), or when pre-aeration is required to passivate *cyanicides*. In the case of cyanicides requiring pre-aeration, adding cyanide to the milling circuit can dramatically increase the total amount of cyanide required.

8. PROCESS CONTROL

No discussion of comminution and classification circuits would be complete without some mention of process control (further details may be found in Chapter 9). Process control consists of a variety of levels, starting with instrumentation and basic regulatory controls. Expert systems and model-based controls generally fall into the category of *advanced process control*. A general hierarchy of typical process control is depicted in Fig. 12.

Thankfully, the literature now has many examples of the clear benefits of installing expert systems. The overriding principle is to control the circuit at peak conditions for nearly all of the time, instead of only a portion of the

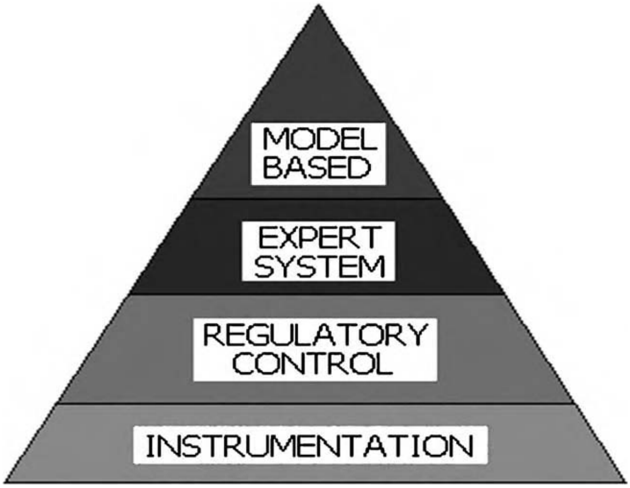

Fig. 12. Process control hierarchy.

time. To attain high utilization, process-control systems must be easily understood, have a good user interface, and be flexible enough to be run during the majority of conditions encountered in routine operation. PTFI's location, staff, and maintenance considerations demand a standardized, robust system (Neale and Veloo, 1997). At the heart of this system is a plant-wide (from primary crushing through concentrate loading) distributed control system. PTFI also uses model-based systems for control of optimum milling setpoints for the SAG circuits. This system, *Dynamic Process Optimization* (*DPO*), was developed internally in collaboration with Rio Tinto Technical Services, and has since been commercialized into Cisa's Optimizing Control Systems (OCS) package. This package was a significant advance over traditional rule-based expert system, as the controller 'seeks' optimum milling conditions that vary as a function of ore hardness, feed size, and other circuit operating conditions. Operation of this system over the rule-based model shows a throughput benefit of over 5% (Mills *et al.*, 2004).

Perhaps as important as the control system is a data historian such as OSIsoft Inc.'s PI system. It is difficult to place a direct process benefit on a data historian, yet when conducting data analyses of plant operating performance and reviewing trends, it is invaluable. Applications include maintenance troubleshooting, condition monitoring, identification of root causes, development of models, regression analyses of different operating regimes, and so on.

9. ALTERNATE GRINDING TECHNOLOGIES

Dry grinding is an important, albeit niche, application in gold-ore processing. For any pyrometallurgical operation, dry grinding is an obvious consideration. Newmont's Carlin mill and Barrick's Goldstrike mill both have roaster facilities fed by Krupp double-rotator dry mills. The double rotator mills consist of a twin-chamber mill (with sides for coarse and fine-milling), with both sides discharging to a common air-classification system. Operation of Goldstrike's system is well described by Buckingham *et al.* (2001). Newmont's Minahasa gold operation employed an Aerofall SAG mill followed with dry ball-milling.

High-pressure grinding rolls are an advancing comminution technology with a number of potential applications. Several studies have considered high-pressure grinding rolls (HPGRs) for applications including inclusion in conventional crushing circuits as well as for secondary pebble-crushing. An interesting feature of HPGR crushing for gold applications is the potential to increase gold recovery in leach as a result of micro-fracturing. This effect is discussed in detail by Baum *et al.* (1997).

10. ORE SORTING

Ore sorting implies coarse-ore separation by a number of technologies designed to reject coarse gangue particles prior to processing. Of course, the oldest technology is hand sorting. Sorting has a number of advantages, not the least of which is eliminating the cost of milling non-value-containing material. Circuit capacity for ore also increases as gangue material is rejected. Arvidson (2003) reviews the most widely used ore-sorting technology, photometric sorting. This technology separates coarse particles based on differing optical properties. Any number of different properties have either been employed or could be employed for ore sorting, including magnetic and radiometric sorting.

Another form of sorting based on selective grinding has also been employed either full-time or occasionally at a number of different operations – rejection of pebbles generated in the pebble-crushing circuit. Pebbles are often less than head grade, and in some cases, barren. In order for this to be economic, the pebbles must typically be quite low grade, as all of the mining, haulage, and a portion of the comminution costs are already sunk, and the contained values must only carry the balance of costs associated with further processing. In some cases, particularly for mill construction or major haul road construction, the pebbles (assuming that there are no environmental considerations) can have significantly higher value as aggregate than as ore.

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The contribution of various parties at PTFI to optimize the comminution circuits has been broad based, and includes mill operations, maintenance, and technical services staff, as well as contributions from staff at both the Grasberg open pit and DOZ underground mines. The combined efforts of staff past and present, and the direct support of Armando Mahler, Rick Coleman, and Darin Lee, have established PTFI as a world leader in comminution practice as well as the world's number one gold producer in 2003.

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II.2 *Concentration*

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Chapter 13

Advances in gravity gold technology

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1. INTRODUCTION

This chapter will describe units, circuits and strategies used to recover gold that is either liberated or present in very high-grade gold particles, referred to as *gravity-recoverable gold*, (*GRG*), as well as gold present in much lower grades in sulfidic particles, typically pyrite and arsenopyrite, that can in their own right be recovered by gravity. These particles will be referred to as *gold carriers*.

Recovery strategies for GRG and gold carriers vary, as only GRG can be substantially recovered at very low-weight recovery into the concentrate, or yield ($<0.1\%$), typical of the type of semi-continuous units used today, whereas gold carriers such as pyrite and arsenopyrite are recovered by continuous units capable of much higher yields, which typically match or slightly exceed the sulfide content of the stream treated.

Gravity separation has been utilized in gold plants as the primary recovery mechanism or alternatively ahead of other downstream processes such as flotation and cyanidation since the inception of mineral processing. A heavy reliance on gravity in the grinding circuit of the Australian gold mines as in 1966 (Elvey and Woodcock, 1966) is dominated by the jig, strake and shaking table, as shown in Table 1.

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Table 1
Examples of gold gravity practice in Australia in the mid-1960s (after Elvey and Woodcock, 1966)

Plant	Capacity (t/mo)	Average grade (dwt/t)	% Recovery of gold based on mill head								% Loss of gold				
			Total	Strakes or jig	Calcine strake	Ore cyan	Conc. cyan	Calcine cyan	Post cyan	Other	Total	Flot. tail	Conc. cyan	Calcine cyan	Ore or post cyan
A1 Consolidated	1,500	17	95	90[a]	—	—	5	—	—	—	5[b]	—	—	—	—
Aust. Development	3,500	25.0	98	15[c]	—	83	—	—	—	—	2	—	—	—	2
Central Norseman	14,500	10.5	96.0	44	—	52	—	—	—	—	4.0	—	—	—	4
Emperor	24,000	8.1	90.5	—	—	49.5	—	41.0	—	—	9.5	7.4	—	2.1	—
Golden Plateau	2,400[d]	8.6	94.0	18	—	76	—	—	—	—	6	—	—	—	6
G.M.K. (Oroya)	35,000	5.9	90.8	5–7	—	—	69	4–10	—	—	9.2	9	—	1–2	—
G.M.K. (Mt. Charlotte)	20,000	3.2	No details yet available												
Great Boulder	35,000	5.9	91.5	—	—	43.0	—	48.5	—	—	8.5	6.3	—	2.2	—
Hill 50	18,000	6.6	95.6	62.1	—	33.5	—	—	—	—	4.4	—	—	—	4.4
Lake View & Star	63,000	5.3	92.5	11.3	17.6	—	—	58.3	3.6	1.7[e]	7.5[f]	—	—	—	7.4
Moonlight Wiluna	2,700	11	97	58	—	39	—	—	—	—	3	—	—	—	3
New Guinea Goldfields	7,500	2.8	93.1	62.4[g]	—	30.7	—	—	—	—	6–9	—	—	—	—
North Kalgurli	30,000	5.0	91.6	12.7	—	—	54.5	18.2	6.2	—	8.4	—	—	2.8	5.6
Peko (Orlando)	4,400	7.8[h]	86	43.0[i,j]	—	—	—	—	—	—	14.0	14.0	—	—	—
Wattle Gully	6,000	6.5	95.3	75.7[j]	—	—	19.6	—	—	—	4.7	2.1	2.6	—	—

[a] By direct amalgamation.

[b] In battery tailing.

[c] Jig and strakes.

[d] Ten shifts per week.

[e] Increase in gold process.

[f] Including 0.1% dust loss.

[g] 943.5% plate amalgamation and 18.9% strake and trap.

[h] Also 1.0% copper.

[i] Also 43.0% recovery of gold in a flotation concentrate assaying 72.0 dwt/t gold and 20% copper.

[j] Recovery by jigging.

The recovery of free and sulfide (pyrite, arsenopyrite and telluride)-associated gold from the primary grinding circuit featured in all these installations. Virtually, every gold mine in Australia incorporated gravity recovery in the primary grinding circuit.

The treatment of the concentrates ranged from full gravity via tables through amalgamation and in many cases cyanidation was used to recover gold from the concentrates. The use of amalgamation was featured in many mines but has since been phased out due to health and environmental issues. Until recently, the only common option was the shaking table, despite its lower efficiency. Rotating devices are also used in a very limited number of plants, such as Round Mountain, Nevada and Marvel Loch, Western Australia. Intensive cyanidation, notwithstanding its higher recoveries, never achieved a high degree of acceptance, possibly because of the lack of a commercial unit.

Issues such as the poor operability, security and maintenance of these circuits combined with rapid advances and the elegance of the carbon-in-pulp (CIP) and carbon-in-leach (CIL) process, capable of achieving very high recoveries, saw a reduction in reliance on gravity as a primary means of concentration. This was amplified by the move towards simplified, low-capital plants with low manning levels and automated processes. This drove down operating costs, which in turn made possible the treatment of lower-grade ores. This is typified by the low-grade oxide orebodies of Western Australia, many with head grades around 1 g/t.

However, some orebodies have been found to have attributes that do not lend themselves to high recovery through the direct cyanidation route. Coarse free gold and gold associated with complex sulfide minerals tend to complicate the cyanidation process. Coarse gold increases the residence time required to achieve high recoveries by cyanidation. Complex metallurgy can cause coatings on gold that render it impervious to cyanidation, while other forms of gold such as gold locked in a sulfide lattice as solid-solution gold or attached to a sulfide particle can report to the tails stream of a conventional cyanidation plant. These problems are generally amplified for the coarse grinds normally associated with low-grade ores. A better understanding of these problems and the development of larger, more reliable gravity units, as well as intensive cyanidation, have heralded a return to gravity recovery. The return, driven by economic considerations, will be detailed in this chapter.

1.1. Economics

The economic benefits of gravity recovery are application-dependent, as shown in Table 2. For more than 95% of all applications, gravity recovery targets GRG to supplement cyanidation or flotation, thereby increasing overall gold recovery by 1–5% and slightly reducing some of the costs associated with carbon stripping and regeneration. Whenever gold carriers are

Table 2
Economic impact of gravity recovery (non-alluvial applications)

Application type	Benefits
Recovery of GRG ahead of cyanidation	Higher overall recovery Lower carbon costs Lower retention times in cyanidation
Recovery of GRG ahead of flotation	Higher overall recovery Better Net Smelter Return (NSR) Lower reagent costs Possible avoidance of cyanidation
Pre-concentration	Lower downstream processing and tailing disposal costs
Scavenging of GRG and gold carriers (cyanidation tailings)	Higher overall recovery
	Coarser initial grind
Partial pre-concentration of gold carriers for intensive cyanidation	Higher overall recovery
	Coarser initial grind

targeted, the benefits are generally higher, as is the cost of the gravity circuit. These applications include pre-concentration (although this is more commonly achieved with flotation – see Chapter 14) and scavenging of gold carriers. A discussion on the use of gravity instead of flotation for pre-concentration is included in Section 2.

Because much of the GRG normally recovered in a grinding circuit would later be recovered in the downstream cyanidation or flotation circuit, accurate estimation of the economic justification of GRG recovery can be difficult. However, overwhelming plant experience shows that additional *overall* gold recoveries are typically achieved when gravity recovery circuits are retrofitted. Recent retrofitting of intensive cyanidation in gold rooms alone has yielded additional overall recoveries of 0.5–1.5%, at sites such as St. Ives and Kundana, Western Australia; Porgera, Papua New Guinea; and Dome Mine, Ontario. Very few of these improvements have been documented in the public domain; when they are (*e.g.* Chong *et al.*, 2004) co-current improvements or changes make it difficult to isolate their exact contribution.

In extreme cases, the economic impact of gravity recovery can be exceptional. Such is the case at the Penjom mine, which suffers from an extremely preg-robbing carbonaceous component. A combination of GRG and gold carrier gravity recovery followed by intensive cyanidation contributed to an increase in overall gold recovery approaching 20% (Lewis, 1999).

2. NON-CENTRIFUGE CONTINUOUS CONCENTRATORS

2.1. Existing practice

The continuous concentrators are defined as those units that receive continuous feed and produce continuous tailing and concentrate streams. The use of continuous gravity concentrators in the gold industry has been limited in the last 20 years because the semi-continuous concentrators have been dominant in recovery of GRG from grinding circuits. However, continuous non-centrifuge concentrators such as the InLine Pressure Jig, shaking tables, conventional jigs, Reichert Cones, and spirals have been utilized, as shown in Table 3.

In most instances, these units have been employed to recover GRG. Reichert Cones are used as pre-concentrators for semi-continuous units or for spirals, whereas duplex jigs have largely been replaced by semi-continuous units in North America, except for alluvial applications. Duplex jig capacity is difficult to assess, but Richardson (1984) reports capacities of up to 280 m^3/h (380 cu. yards/h) for a 5.49 m (18 ft) diameter circular jig, compared to 37 m^3/h (49 cu. yards/h) for a 4-cell duplex jig, each cell 1.14 m^2 (3.5 sq. ft) in surface.

The newest of the non-centrifuge continuous units is the InLine Pressure Jig (Gray, 1997), which has been utilized in the recovery of GRG and gold carriers. This unit has the advantage of being able to accept a wide range of feed size while at the same time adding very low levels of dilution water to the grinding circuit. Also, a true *saw tooth* stroke is generated by a hydraulic

Table 3
Non-centrifuge gravity applications

Unit	Capacity (dry t/h)	Application	Site
InLine pressure jig	2–100	Mill discharge/ cyclone underflow	Beaconsfield, Tasmania
Duplex/circular jigs	$<190\,m^3/h$	Mill discharge/ cyclone underflow	Alluvial mining
Reichert cones	50–250	Leach tails	Bjorkdal, Sweden Omai, Guyana
Spirals	2–4 per start	Cyclone underflow	Granites, Northern Territory Round Mountain, Nevada
Shaking tables, cones and wheels	0.3–1	Concentrate cleaning	Gold rooms where intensive cyanidation is not used

drive system that enables control of all critical pulse parameters. The unit is capable of recovering finer mineral than conventional jigs at high throughput rates per screen surface area.

The complex ores, as defined by the poor recovery in a conventional cyanide leach circuit, tend to have a larger component of the gold associated with the sulfide minerals or gold carriers. Higher yields are therefore needed.

The use of continuous gravity concentration in the grinding circuit for the purposes of sulfide and gold carrier recovery is increasing. Gravity removal of gold and gold carriers from the grinding circuit offers many benefits over flash flotation, such as reduced operating cost and much coarser recovery. The maximum recovery size limitation on the flash circuit can be as low as 150 μm. For many ores it can be critical to recover the GRG and gold carriers from the grinding circuit before it gets to this size range. As well, flotation chemicals create surface chemistry issues both with gold particles and activated carbon. As a result, gravity recovery is often preferred to flash flotation, or operated co-currently, as exemplified by the Beaconsfield plant in Tasmania (see the *Plant examples* part of this section).

2.2. Optimum yield and recovery

The targeted yield is determined by the distribution of specific gravities (SGs) in the ore and the SG of the heavy minerals to be recovered. From these a cut point, which represents the center of the separation, is chosen. This point is expressed as a density (specific gravity) or typically as the *effective density of separation*. For instance, the cut point may be set at a SG of 3.2. Allowance for imperfection in the liberation of the mineral and unit recovery of the concentrator means that it is generally necessary to produce higher than optimum yields to force higher recoveries. Examples are provided in Burt (1984).

In order to force higher yields to concentrate the cut point is reduced, resulting in a lower grade concentrate but at a higher recovery. In the case of gold, with an effective SG between 16 and 19, the density differential is high, which should in theory result in a simple separation. However, the key factor in gold's response to gravity is its aspect ratio or shape factor. Whether comminution is carried out in tumbling mills or in the natural environment in which alluvial gold is found, malleable gold particles eventually assume a shape with a high aspect ratio, variously identified as flakes, platelets or lamellae. This shape, combined with the natural hydrophobic nature of gold, impacts severely on its potential for gravity recovery. On the other hand, sulfides, inclusive of gold carriers, tend to have a considerably lower SG but grind in a far more equi-axed fashion, which in turn aids in gravity recovery. This relationship of factors adds to the *relative density* or in other words the way in which a particle acts when settling in a fluid after all characteristics of density, aspect ratio and surface conditions are considered.

Fig. 1 shows a typical yield/recovery curve that represents the response of the ore to a shaking-table separation. The left-hand side shows the gold recovery relative to the yield or mass recovered to concentrate, and the right-hand chart shows the reduction of gold grade in the concentrate as the yield is increased. The *sink/float* result with a SG of 2.9, which is indicative of a 'perfect' separation, is also shown. Results of Fig. 1 are below those normally obtained by heavy liquids, not only reflecting the limitations of single *g* separation, but also the size, shape and liberation issues previously discussed.

The better an ore responds to gravity the further the curve will bend to the top left corner of the chart. The initial 'low-yield' points tend to represent the GRG component of the ore while the initial curve represents the lower density particles and the near-density material, *i.e.* the gold carriers.

2.3. Testwork

In order to effectively characterize the overall gravity gold recovery potential of an ore, *i.e.* recovery of all GRG and gold carriers, it is not possible to use the more conventional measurement means applied in bulk minerals such as coal and iron ore where the traditional method of E_p curve is applied. It was therefore necessary to develop a procedure to accurately measure any ores response to gravity recovery with relation to yield. The technique developed by Gekko was initially developed to emulate continuous recovery from an ore in the grinding circuit. The test was derived from the McGill GRG test (Laplante *et al.*, 2001). The key is a step-by-step grind followed by recovery. As with the GRG test, the ore is first ground then a separation is carried out on a small lab-scale shaking table (as opposed to a semi-continuous centrifuge). Typically three separate grinds and recoveries are carried out with all concentrates being recombined and tabled once again to

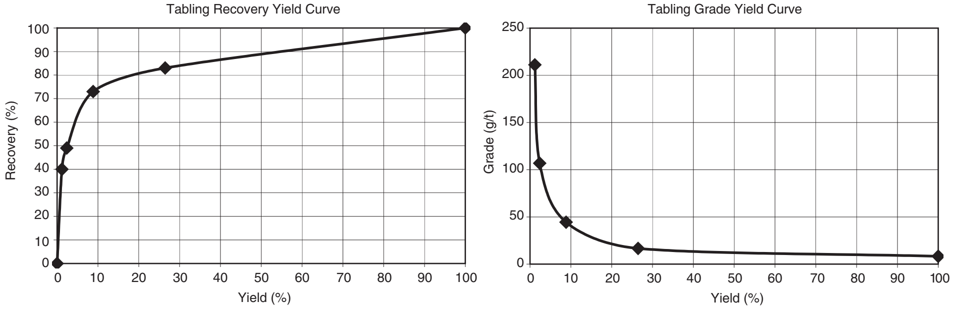

Fig. 1. Typical laboratory yield recovery and yield grade curves.

produce four concentrate streams and a tailing. The products can be sized at any time to assess the size-by-size recovery at any point in the process.

Typically a separate exercise is carried out to assess the liberation. The ore is ground to a pre-determined size and then tabled to produce four concentrate streams and a tailing product. Usually as many as three separate grinds (1,000, 500 and 150 µm) are tested to develop a good understanding of the potential liberation and gravity amenability at various size distributions. The ore is first ground and then tabled. The products are all sized and assayed separately to give a size-by-size recovery. The yield/recovery curves are then generated along with the yield/grade curves and the size/recovery curves. This information is then utilized along with the Gekko recovery model to simulate overall recovery of gold and gold carriers from the grinding circuit, producing information related to particle size, mass-balance and flows in the overall circuit.

2.4. Plant examples

2.4.1. Beaconsfield gold mine

Beaconsfield Gold Mine in Tasmania operates a gravity recovery circuit ahead of a flotation plant in order to maximize the gold recovery in the total plant. The gravity circuit plays a critical role in the recovery of gold from the total circuit as the flotation recovery alone drops when the gravity recovery is off-line. Utilizing both InLine Pressure Jigs and centrifugal concentrators allows for a very strong combination of complementary technologies. The gravity circuit at Beaconsfield is made up of an InLine Pressure Jig IPJ1500 that is fed by a separate pump located at the mill discharge. The tailings from the IPJ return to the cyclone feed pump and the concentrate feeds a Knelson Concentrator CD20 that cleans the IPJ concentrate to produce a high-grade concentrate. Parallel to this circuit is a Knelson Concentrator CD30 that is also fed from the mill discharge hopper and also produces a high-grade concentrate. The CD30 tailings are returned to the flash flotation feed ultimately, limiting free gold reporting to the subsequent bacterial oxidation and leaching circuits.

The two high-grade concentrates are tabled daily on a Gemini table to produce a smeltable-grade concentrate. The Gemini table tailings then report to the concentrate regrind circuit where further gravity separation is carried out with a small InLine Spinner ISP02 and a Knelson CD12. These concentrates also report to the Gemini batch storage for cleaning.

An independent survey shows the unit recoveries and performance at the time of the survey. Table 4 shows the recovery by size for each unit in the primary circuit, and is useful in understanding the capabilities of each technology.

The combination of continuous concentrators such as the IPJ and flash flotation is a powerful tool when the two recovery charts are combined, as

Table 4
Summary of unit performance at the Beaconsfield mine

Unit	Feed stream	Feed rate (t/h)	Unit recovery (%)	Rec. rate (g/h)	Upgrading ratio	P_{80} gold recovered (μm)	Gold distance[a] (%)
InLine pressure jig	Mill discharge	60	26	382	4:1	320	52
20" Knelson	IPJ concentration	4	52	202	72:1	320	28
30" Knelson	Mill discharge	60	18	209	110:1	320	28
Flash flotation	Knelson CD30 tail	60	17	161	9:1	106	21
Cyclone[b]	Mill discharge	120	93	2211	1.2:1	320	22

[a] As a function of mill feed gold.

[b] The cyclone is treated as a concentrator where 'concentrate' is the cyclone underflow and recovery is the cyclone underflow/cyclone feed.

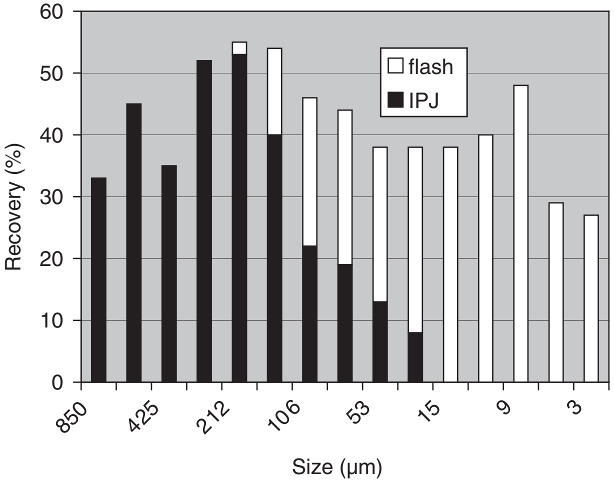

Fig. 2. Size-by-size gold recovery for flash flotation and InLine Pressure Jig (IPJ) at the Beaconsfield Mine.

shown in Fig. 2. The size distribution of the gold recovered by the IPJ significantly reduces from the 106 μm range, from which it can be seen that the flash flotation recovery increases significantly. The complementary nature of all the devices and their abilities is important as it can lead to a considerably increased overall recovery.

2.4.2. St. Ives gold mine

St. Ives Gold Mine has recently installed a new 4.5 Mt/a mill with a single-stage semi-autogenous grinding (SAG)-milling circuit. The circuit has a heavy reliance on gravity due to the coarse nature of the target grind size and as such has installed InLine Pressure Jigs in the grinding circuit to recover both GRG and gold carriers. The IPJ concentrate reports to a Falcon SB concentrator for GRG recovery, with the tailing of the Falcon reporting for regrind in a tower mill before returning to the leach circuit. The expected overall gold recovery benefit from the IPJ sulfide circuit is of the order of 3%.

The circuit will also run two Falcon SB units in the cyclone underflow for GRG recovery directly from the circuit. The concentrates from all Falcon units will report to an InLine Leach Reactor for final recovery.

The circuit design has had a heavy focus on gravity and the complete gravity circuit has been integrated into the mill psychology. With a greater reliance on gravity the residence time in the cyanidation circuit is reduced and hence the overall plant capital is reduced. The overall recovery is also expected to rise owing to the symbiotic relationship between leaching and gravity.

3. CENTRIFUGE UNITS

3.1. Existing practice

Uses of centrifuge separation for gold include recovery of GRG using semi-continuous units and, to a lesser extent, recovery of both GRG and gold carriers using continuous units (Laplante, 2002). Table 5 lists, in descending order of abundance, the various units, how they are used and examples of each application. No graphic representation of these units is provided here; rather, the reader is directed to the manufacturers' websites, from which figures and demonstration videos can be downloaded. The semi-continuous units include 99% of gold applications, and will be the only ones discussed at length here. These units run continuously over a recovery cycle, producing a continuous tailing product. At the end of the recovery cycle, the feed is interrupted and the concentrate recovered. This limits the yield of these units typically to less than 0.1%, and given that much of that is recovered rather unselectively at the beginning of the recovery cycle, effective yield is typically less than 0.05%.

Virtually all applications of semi-continuous units are aimed at GRG recovery, because the low yields typically achieved by these units preclude recovering a significant proportion of gold carriers. Most other applications would target the recovery of equally high-density, very low-grade species such as platinum group minerals.

The most common application of semi-continuous units is the recovery of GRG from the circulating load of grinding circuits. For circuits with two circulating loads, the coarser circulating load is usually targeted, unless it is extremely coarse, such as for SAG mills in closed circuit with cyclones.

Table 5
Typical centrifuge units used for gold recovery

Unit	Top capacity (dry t/h)	Application	Application and website
Knelson concentrator XT	1,000	Recovery of GRG from cyclone feed, ball mill discharge, cyclone underflow, flash flotation concentrates, table tailings and alluvials	See manufacturer websites: www.knelson.com www.concentrators.net
Falcon concentrator SB	400		
Gekko's spinner	30	Recovery of GRG from jig concentrate	Jubilee Gold Mine Western Australia www.gekkos.com.au
Falcon continuous concentrator	100	Recovery of GRG and non-GRG from cyclone overflows	Kettle River, Washington
Kelsey jig	80	Recovery of GRG and non-GRG from cyanidation residues	Granny Smith Western Australia www.rochemt.com.au
MGS	4	Recovery of a gold-rich phase from flotation concentrates	www.natcogroup.com
MeGaSep	30		

Any of the three streams of the circulating load can be targeted: cyclone feed, cyclone underflow and ball-mill discharge (Gray, 2004). Table 6 shows their respective advantages and disadvantages as bleeds. Although ball-mill discharge is probably the most efficient stream to target, with a maximum of GRG liberation and grade, cyclone feed is often the most cost effective, as it minimizes cyclone height and the number of pumps needed. Thus, the choice would probably hinge on the economic incentive of gravity recovery: the more significant the incentive, the more recovery from ball-mill discharge is favoured. The best option would also hinge on ease of operation and availability: a recent conversion of a circuit in Western Australia from a sluice on the ball-mill discharge to cyclone underflow resulted in a significant gain of availability and overall gravity recovery.

Table 6
Options for GRG recovery from circulating load

Criterion	Cyclone underflow	Cyclone feed	Ball mill discharge
Proportion of circulating load treated	Best	Worst	Best
Ease of screening[a]	Worst	Best	Best
Best liberation	Average	Worst	Best
Minimizing capital and operating costs	Average	Best	Worst
Minimizing short-circuit[b]	Average	Worst	Best

[a] Fine product, low percent solids.

[b] Maximizing the proportion of feed that is both ground and classified in-between passes.

When shoehorning a gravity circuit into an existing grinding circuit, it is recommended to base the choice of bleed on ease of layout and operation rather than proposed performance. Simulation of various options does not show dramatic differences in overall gravity recovery, and ease of operation (and by extension circuit availability) is a much more significant issue.

If short-circuiting is defined as the proportion of material that is fed to gravity twice without being classified and ground, then clearly cyclone feed is the option that maximizes short-circuiting, while ball-mill discharge completely eliminates it. As more and more of the circulating load is treated, the probability of short-circuiting increases and the ball-mill discharge option becomes the best one. Another alternative is to process the entire cyclone feed, but this requires pumping the material twice, and is probably the most expensive option; it could only be justified if the degree of GRG liberation in the primary mill discharge is high. It would be chosen if the economic incentive of gravity recovery is such that recovering GRG that would report to cyclone overflow is critically important. This would only be used under exceptional circumstances, such as when a very coarse grind is targeted.

Although recovery of gold carriers is far more frequently achieved with non-centrifuge units, two continuous centrifuge units have seen applications for gold recovery, be it GRG or gold in gold carriers. At Kettle River, a Falcon Concentrator C2500 is used to recover 17% of the gold and 12% of the sulfur in 7% of the cyclone overflow. The material is intensively leached in the first tank of the cyanidation train; the Falcon tail is added to the second tank of the train. Increases of recovery between 0 and 5% are reported.

The second application is the recovery of GRG and gold carriers from the tailing of the cyanidation circuit at Granny Smith (Butcher and Laplante, 2003). The tailing stream is cycloned and part of the cyclone underflow is fed to three Kelsey J1800 centrifuge jigs (typically two are running), which produce a concentrate further upgraded in spirals. An extra 4% in gold recovery is achieved.

3.2. Testwork

This section will focus on GRG recovery, which is the dominant application of centrifuge units for gold. Gold-carrier applications, such as the two just described, would usually require piloting or plant trials (Laplante and Spiller, 2002).

The recovery of GRG from flash-flotation concentrates is relatively simple to test at bench scale, but does require feed material, which is usually obtained by piloting of the flotation unit. The intended specific feed rate (*i.e.* feed rate per unit of concentrating surface) at full scale should be used; it is usually much lower than that of units used in closed circuit to maximize single-pass recovery.

Testing for recovery of GRG from grinding circulating loads is not as easily achieved, as this application is one of sequential liberation and partial recovery. Recovery of GRG is a function of the ore, the grinding circuit (grinding kinetics and classification) and the gravity circuit (sized primary and secondary recoveries). It is argued here that trying to take into account all three elements in a simple bench-scale test to accurately predict how much gold will be recovered is virtually impossible. Rather, two types of bench-scale tests should be performed.

The first type is one that would characterize the GRG of the ore, from which gravity recovery can be modelled or predicted taking into consideration the existing (brownfield) or proposed (greenfield) grinding and gravity circuits. The GRG test (Laplante *et al.*, 2001) is the standard test to achieve this. Gold is sequentially liberated and recovered using a laboratory centrifuge unit. The sequential nature of the test preserves the natural size distribution of the gold, which is important in assessing potential gravity recovery.

The second type is one that produces an appropriate feed for testing recovery downstream of gravity. For these tests, it is important to remove the approximate amount of GRG that would be removed by an economically efficient gravity circuit, rather than all GRG. The typical approach is to grind 10–20 kg of feed to final size, process with a laboratory centrifuge concentrator and clean the separator concentrate by hand-panning or with a Mozley laboratory separator (MLS). The centrifuge and cleaner tailings are combined for further testing. The gravity recovery achieved in this test is lower than the actual GRG content, but it is a better reflection of what would be achieved at plant scale.

A simpler version of the GRG is being developed that would resemble the second type of test. This test would use 20 kg of feed ground to final size, and

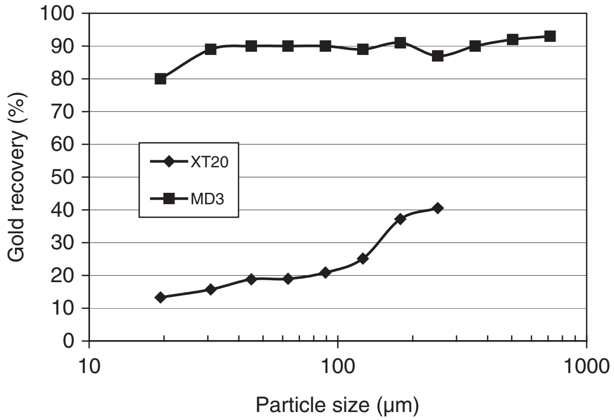

Fig. 3. Comparing bench-scale and full-scale gold recovery for Knelson Concentrators (MD3: 3-inch lab unit at low specific feed rate; XT20: 20-inch plant unit at high specific feed rate).

would be processed once with a laboratory centrifuge unit. Its concentrate would not be cleaned if used for GRG purposes only. The original GRG size distribution would be inferred from that measured. The tailing stream could be used for further testing.

Piloting of gravity recovery is not without its difficulties, as the recovery effort of the projected plant is not easily reproduced (the tendency is for a much more effective gravity circuit at pilot scale). It does provide for a very accurate estimate of the grade of the material tested and is suitable for complex downstream flowsheets (*e.g.* flotation of low-grade copper or refractory ores).

An important and often overlooked point is that test gravity data, to be effectively scaled up to prediction of pilot performance, should have a modicum of sized information, as fine gold is much more easily recovered at bench scale than full industrial size. This is illustrated in Fig. 3, which shows recovery vs. particle size for GRG and total gold at full scale and at typical feed rates. GRG being defined as gold that is recovered by a bench-scale unit operated in optimized bench mode, the GRG full-scale data of Fig. 3 is also a measure of how much of the bench-scale recovery the full-scale unit achieves. It is clear that this proportion drops dramatically as particle-size decreases.

3.3. Unit and flowsheet selection based on test results

Sized data generally make it possible to select and size an adequate circuit flowsheet. The questions to be answered are as follows:

- Which stream should be selected for gravity recovery?
- For primary recovery, should centrifuge or non-centrifuge units be used?

- For secondary upgrading, should intensive cyanidation or tables be used?
- How fast should centrifuge units be operated?

The first question has been addressed. For recovery of GRG or non-GRG above 100 µm, non-centrifuge units can achieve excellent recoveries. Below 100 µm, centrifuge units are warranted provided the amount of finer GRG or gold is substantial. Although coarse GRG can be ground into finer recovery if not recovered, the fine GRG may not accumulate in the grinding circuit if classification is coarse, making centrifuge units less attractive. Thus, coarse classification and coarse GRG favours the use of non-centrifuge units. Another approach, which is discussed in Section 2 and practiced at Beaconsfield, is to use non-centrifuge units operated at a high yield as pre-concentrators for semi-continuous units (see Table 4). Increasing yield has a beneficial effect on gold recovery, particularly at fine size.

Non-centrifuge units are typically not as selective and tend to recover significant amounts of dense minerals, as they are operated at much higher yield than the semi-continuous centrifuge units. This can make downstream treatment difficult; alternatively, gold carriers are also recovered, and can therefore be given preferential treatment, such as regrind, intensive cyanidation or both.

The above logic equally applies to rotating speed for centrifuge units. When treating circulating loads, the cut size of GRG (*i.e.* classification) will determine the extent to which fine GRG, which requires higher rotation velocities, accumulates in the circulating load. A coarse cut-size implies that rotational velocity should be lowered, particularly for the recovery of coarse middlings (Dunne, 2004). At the Bulyanhulu mine, the introduction of a contact cell competing with two Knelson Concentrators XT30 lowered the gravity recovery by floating relatively fine GRG. Gravity recovery was restored when rotating velocity was slowed down and a regrind mill commissioned in the gold room.

3.4. Modelling for unit selection, circuit design and optimization

Specific questions about circuit design are best answered using modelling and simulation:

- Should gravity recovery, flash flotation or both be used?
- How many recovery units should be used? How much should they be fed?
- How will the size distribution of gold particles be affected by gravity/flotation recovery?
- From which stream should the bleed to the gravity circuit be extracted?

The issue of flash flotation vs. gravity recovery normally arises for base metal ores, where the main recovery method is flotation. The interaction of flash flotation and gravity recovery has been discussed by Laplante and Dunne (2002). A recent presentation (Hilliers, 2003) discussed the choice for the Fimiston mill in Western Australia, where gravity recovery was finally chosen to minimize the amount of GRG coarser than 100 μm reporting to the cyclone overflow. Finer classification and GRG would have favoured flash flotation.

The number of recovery units is an issue that has received little attention until recently. Simulation shows that gravity recovery is roughly proportional to the logarithm of the number of units used. In other words, unless the units are grossly undersized, the contribution of the fourth unit to overall recovery is minimal, *e.g.* less than *one-fourth* that of the first unit in a recent simulation. The second unit's contribution is about half that of the first unit. In such a situation, the third unit would be justified mostly to minimize the impact of one of the first two being unavailable, in cases of strong economic incentive for gravity recovery. For the typical modern grinding circuit with one SAG mill and two ball mills, between two and four gravity units would be adequate, depending on the economic incentive of gravity recovery.

Plant layout should make it possible to operate screens and centrifuge units in a flexible manner. A distributor box between the screens and the units would achieve such a purpose, as screens and centrifuge units are regularly shut down for clean-up, concentrate removal or maintenance.

Unit capacities as posted on manufacturer's website can be misleading, or at the very least confusing. Centrifuge units operated in closed circuit do not behave like other gravity units in that feed rate can vary significantly. As feed rate increases, recovery decreases to reflect the reduced retention time, much like a flotation cell. Thus, a Knelson Concentrator XT30 fed at 10 t/h would recover about 90% of the GRG (and virtually no non-GRG); the same unit fed at 60 t/h would recover about one-third of that, but at constant feed grade, this is twice as much GRG. Fig. 3 shows that the drop in recovery with increasing feed rate (per surface concentrating area) is mostly at fine particle-size. For closed-circuit applications, it is generally better to use higher feed rates (*e.g.* up to 80–100 t/h for a Knelson Concentrator XT30) to maximize gold production rather than unit recovery. Open-circuit applications, such as recovery from flash-flotation concentrates or scavenging gold-room tailings, would use much lower feed rates.

The amount and size distribution of the GRG reporting to the cyclone overflow is affected by the number of gravity-recovery units used, but the effect, much like actual gravity recovery, has a rapidly diminishing return. Fig. 4 shows that it is difficult to justify more than two units on this basis, provided that the units are of adequate capacity. With capacities of up to 500–1,000 t/h for one of the manufacturers, this should always be the case.

Existing centrifuge models lack the accuracy to fully take into account operating parameters, such as feed density, to particle size or rotating

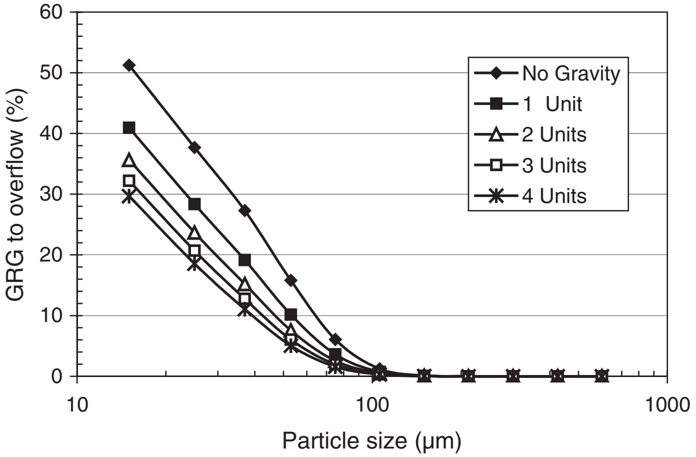

Fig. 4. Cumulative GRG size distribution in a cyclone overflow as a function of the number of recovery units in the circulating load (100% original GRG in the ore).

velocity, although bench-scale work with synthetic and actual ores suggest significant effects. Planned pilot-plant testwork in the near future should provide much of the missing information, and will make it possible to fine tune circuit design.

4. GOLD ROOMS: TABLING AND INTENSIVE CYANIDATION

Primary concentrators produce a gold concentrate stream that is too low in grade for direct smelting. The use of secondary concentration to further upgrade the concentrate is required. Throughout the world it is most common for gold to leave site in the form of gold bars smelted and poured on-site to *doré*. However, the smelting facilities on most sites are relatively small in capacity and require a very high-grade feed such as calcined steel-wool with a gold grade that typically ranges between 20 and 50% gold. The gold grades produced from primary gravity devices can range from as low as hundreds of grams per tonne to a maximum of 5%, or 50,000 g/t gold. In every case known to the authors, an intermediate concentration step is necessary to achieve a grade that is considered cost effective to smelt on site.

4.1. Table-based recovery

In mills devoid of a cyanidation circuit the use of intensive cyanidation may be impossible or undesirable. Some gold minerals, such as maldonite [Au_2Bi], may also respond poorly to cyanidation. The traditional table-based gold rooms must then be used. These can recover anywhere from 40 to 97%

of the gold in the primary concentrates. Very high recoveries are normally achieved when the following conditions are met (Laplante *et al.*, 2002):

1. Concentrates are recovered into tanks with effective level control.
2. Tables are constantly supervised by a dedicated operator.
3. Feed rate to the table is slow and controlled.
4. Recycling of middling streams is practised.
5. The tables are equipped with effective tramp iron removal.
6. A regrind mill is provided if the primary concentrates are not fully liberated, to process the middling streams.
7. A centrifuge is used for scavenging the gold-room tailing stream.
8. For ease of operation, headroom should be plentiful.

The regrind mill not only liberates GRG middlings, but it also grinds sulfides present in middlings into particles that are readily rejected when reprocessed on the tables, while leaving the gold largely untouched. The reground stream is extremely easy to table.

Fig. 5 shows the size-by-size table recovery from a survey at Bronzewing Gold Mine in Western Australia. The table shows high recoveries in the 75–106 μm fraction, but with a very steep drop-off in the other size fractions. Table recovery is difficult to accurately measure with the very high grades present in the concentrate stream and the difficulties associated with the sampling of the long tailings board and transient performance. Nevertheless, extensive testwork on table tailings (Laplante *et al.*, 2002) has shown that in the vast majority of cases, the gold lost to table tailings was GRG that could easily be recovered by gravity recovery, strongly suggesting that low gold-room recoveries were associated with gold-room flowsheet and practice rather than ore type.

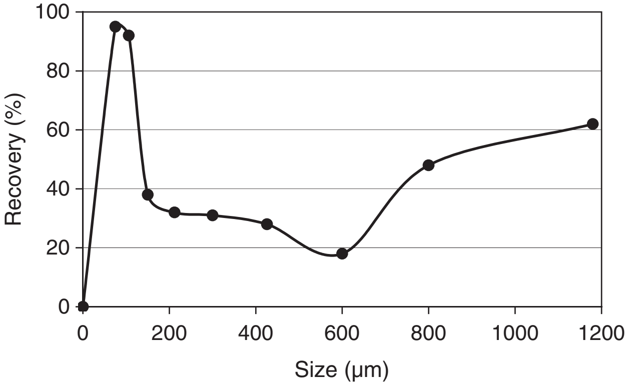

Fig. 5. Size-by-size gold recovery for tabling at the Bronzewing Gold Mine.

Although table-based gold rooms can achieve high GRG recovery, gold associated with tramp iron is not normally recovered, and the usual security issues associated with manipulation of high-grade gravity concentrates apply. Some concentrates also contain mercury or arsenopyrite, which makes smelting of table concentrates difficult. This makes intensive cyanidation the preferred route.

In order to understand the effects of low recovery achieved by some shaking tables, a test was developed by Paul Fallon at Browns Creek Mine in New South Wales. The overall aim of the test was to quantify the effect of a high-grade gold stream being returned to the grinding circuit from the table tailings during the tabling process. The paradigm at the time was that gold, due to its high SG, naturally recycled to the cyclone underflow until it was either recovered by gravity or ground into finer gold. This test effectively showed that a significant proportion of the gold that returned to the gravity circuit reported *immediately* to the leach feed.

A simple survey was carried out whereby the cyclone overflow and underflow were sampled before, during and after tabling. Typical results are shown for the cyclone overflow at the Bronzewing mine in Fig. 6. The cyclone overflow is at steady state prior to the tabling of the gravity concentrates. As soon as the tabling begins the grade of the cyclone overflow rises and remains at elevated levels until tabling is completed; it then falls back to the original grade prior to tabling. The bulge of Fig. 6 represents an extra 10 kg of gold being sent to the CIP circuit during the tabling process alone.

With a reliable cyanidation model, data such as that of Figs. 4 and 6 can be used to calculate the effect of tabling on the grade of the CIP circuit tailings stream. Such spikes normally result in increases in cyanidable gold losses,

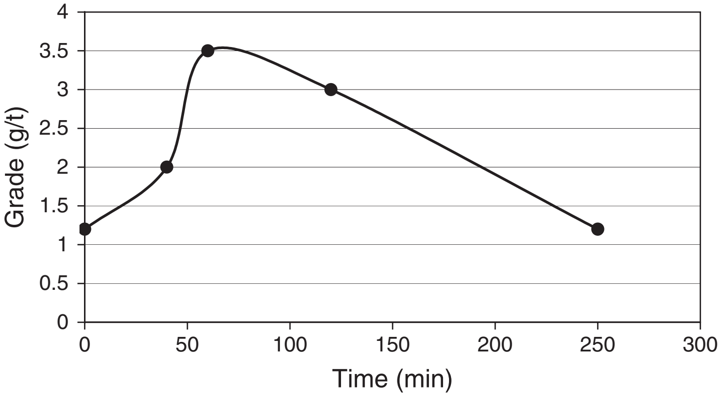

Fig. 6. Effect of tabling on the cyclone overflow grade at the Bronzewing Gold Mine (tabling starts at time zero).

and are a measure of the potential of intensive cyanidation to increase overall recovery.

4.2. Intensive cyanidation

The limitations of tabling have resulted in the swift acceptance of intensive cyanidation; many mines have converted from tabling to intensive cyanidation since 1998, when the first commercial unit, the InLine Leach Reactor (ILR), was introduced by Gekko Systems (Gray and Katsikaros, 1999). This unit, as well as the other commercially available intensive cyanidation unit, the Acacia reactor (Lethlain and Smith, 2000), is fully automated. Typical recoveries of greater than 96% are achieved. The security issue is diminished as the gold is only seen and handled in final recovery from the electrowinning cell at the end of the process. Table 7 lists the three types of intensive cyanidation units that are commercially available.

The two batch-intensive cyanidation units typically process the concentrate from semi-continuous centrifuge units: these products have a much higher grade, typically 2,000–20,000 g/t, but typically less than 12 t/d are produced.

The ILR system is based on a rolling-drum technology and utilizes high cyanide (> 0.5% NaCN) and oxygen (> 20 ppm DO) concentrations. This, combined with the relatively high shear generated in the drum with the particle/particle interaction and the high rate of solution replacement at the particle surface, achieves extremely rapid leach kinetics. Any of the common and exotic oxidants can be used in the ILR but the lowest-cost reagent is oxygen.

Table 7
Intensive cyanidation units

Unit	Capacity (t/d)	Concentrate grade (g/t)	Application	Site
Batch inLine leach reactor	0–12	500–50,000	Low-volume/ high-grade gravity and flotation concentrates	St Ives Gold Mine Western Australia
Continuous inLine leach reactor	0–240	30–1000	High-volume gravity and flotation concentrates	Bibiani Gold Mine Ghana
Acacia reactor	0–6	500–50,000	High-grade gravity concentrates	Union Reef Western Australia

The concentrates from the primary recovery device report to the feed cone for de-watering, with the water slowly released to allow settling, reduce fine gold loss and returning to the milling circuit. Solids are stored in the feed cone until the beginning of each leach cycle.

4.2.1. The batch inline leach reactor

The batch (ILR), shown diagrammatically in Fig. 7, works on the principle of the laboratory bottle-roll to keep the solids in contact with the liquor. A horizontal drum rotating at low speed with a set of specially designed baffles and an oxygenation system for maximum leach performance is utilized for the reaction. Residence time is predicted in the laboratory and controlled by leach cycle time. During leaching, solution is continually re-circulated through the solids from the solution storage tank to ensure that a fresh supply of reagents, including oxygen, is always available for leaching.

At the completion of the leach cycle the pregnant solution is clarified and then pumped to the electrowinning circuit. Barren solids are emptied by reversing the drum rotation and pumped to the milling circuit. Pregnant liquor is pumped to the electrowinning circuit where it can be recovered in a dedicated electrowinning cell or mixed with the main elution solution. The barren solution from electrowinning is then pumped to the CIL/CIP circuit (optionally to the ILR) to reuse the residual cyanide.

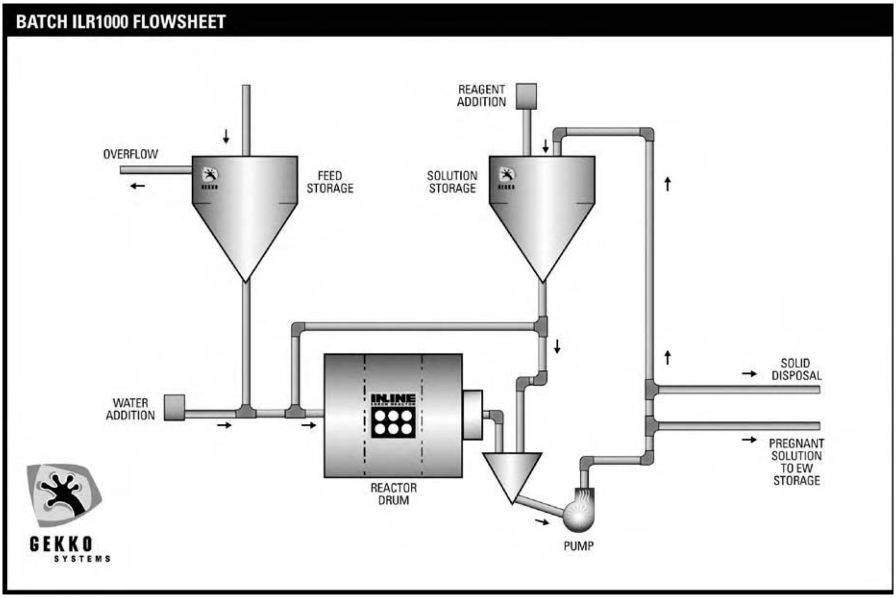

Fig. 7. Simplified diagram of the ILR batch unit.

The batch ILR accomplishes this by cycling through discrete steps. These steps are:

1. Load the concentrate into the reactor drum.
2. Adjust the initial solution volume and add required reagents.
3. Leach by recirculating the solution through the reactor drum.
4. Drain the drum and with flocculant clarify the pregnant solution and pump it to the solution storage tank.
5. Wash the solids with water.
6. Drain and clarify the wash water; direct it to the solution storage tank.
7. Empty the solids from the reactor drum and transfer them to the grinding circuit.
8. Drain the remaining water to the grinding circuit.
9. Transfer the pregnant solution to the electrowinning circuit.

The operating cost for these units depends on the gold grade in the concentrate. This is US$0.70 per ounce recovered for the ILR100BA at the Target Mine in South Africa (Botha *et al.*, 2004). The calculated operating cost can be derived from the testwork as cyanide consumption is the major component.

4.2.2. Acacia reactor

The second batch unit available is the Acacia Reactor, which utilizes a fluidized static bed in order to leach the solids. A schematic view is shown in Fig. 8. The concentrates are deposited in the conical leach vessel on top of a distributor matrix. The solution is made up in an agitated tank and pumped through the distributor and into the leach vessel. The solution flows through the bed and leaching is achieved. This unit utilizes a powerful oxidant such as *Leachwell GC* to provide the oxidant to the leach. Solution is recovered after the leach period between 24 and 72 h and sent to direct electrowinning for gold recovery.

1. The semi-continuous unit concentrate produced over a 24-h period is transferred from the storage cone to the reactor.
2. The concentrate is deslimed over a period of 30 min; slimes are returned to the grinding circuit.
3. The leach solution is mixed in the reagent tank and heating the solution is recommended. Reagents include NaOH, NaCN and *Leachaid*©.
4. The leach solution is used to fluidize and intensively cyanide the concentrate.
5. Fluidization is stopped. The pregnant solution is recovered and the solid residue washed and returned to the grinding circuit. Some of the coarser and denser material, typically grinding ball chips, must be physically removed.

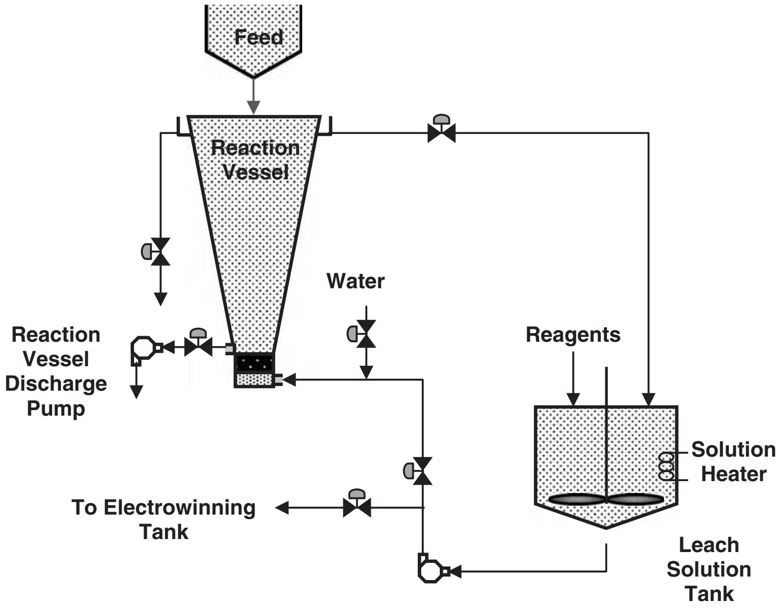

Fig. 8. Schematic representation of the Acacia reactor.

6. The pregnant and wash solutions are electrowon, then directed to the CIP circuit.

4.2.3. *Continuous inline leach reactor*

The continuous ILR units, schematically shown in Fig. 9, handle higher volumes of what would typically be lower-grade concentrates from continuous units such as a spiral, an InLine Pressure Jig or from flotation devices such as flash unit or contact cell, and more recently, as the final recovery step for the Gekko Gravity Float Leach (GGFL) only circuits. The gold grade of these concentrates can be as low as 30–40 g/t. The continuous units have been manufactured with capabilities to handle solids feed rates up to 10 t/h and larger units will be produced.

The system is designed for high leach recovery in the continuous system, with leaching and gold recovery from solution operating in parallel. The key to the operation is the agitation of the solids and the maximized oxidant additions that are achieved with either oxygen injection or the addition of peroxide to produce elevated dissolved oxygen (DO) levels in the solution. The solution is cycled through the unit at very high flowrates relative to the solids. The solids are held in the drum and are controlled in a similar fashion to an overflow mill. The solid is only forced out of the drum by the new solid being fed into the drum. Therefore, a resident mass is set up and the solution flows across and through the solids mass. The solution flows to the clarifying cone

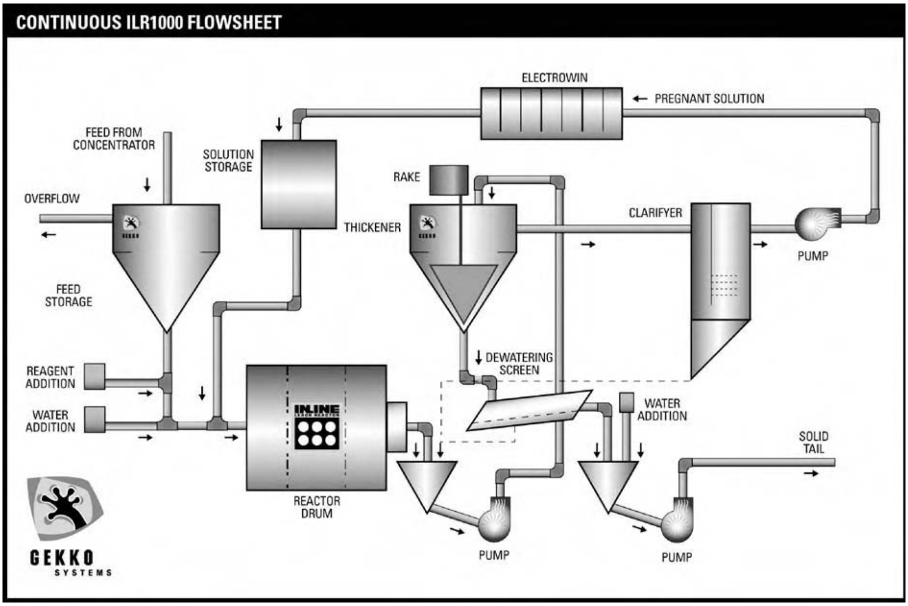

Fig. 9. Schematic of the ILR continuous reactor.

where flocculant is added and the solids settled. The clear solution flows to direct electrowinning, resin or carbon for gold recovery. The fresh reagents are then added to the solution prior to its recycling to the feed of the leach drum.

The GGFL circuits, a recent development, use gravity followed by flotation as the scavenger and are capable of upgrading simple ores with a very high recovery in many cases, producing a throw-away tailing, which comprises the bulk of the ore, and is easily disposed, because of the very low sulfide and zero cyanide content. The continuous ILR is then used to treat the concentrate. The continuous ILR is capable of producing a simple circuit with very high recovery. This also eliminates the requirement for cyanidation of the bulk of the ore and reduces the complexity of tailings discharge and storage. Cyanide consumption is significantly reduced. Several plants, such as the Bendigo bulk sample plant, are currently operating or in the final design stage (Gray *et al.*, 2003).

5. MEASURING METALLURGICAL PERFORMANCE

The measurement of unit efficiency of any concentrator in a gold circuit should follow these fundamental rules:

- Characterize performance on a size-by-size basis.

- Ensure that the sampling, sample processing and assaying protocol minimizes error variance.
- When measuring GRG recovery, separate GRG from non-GRG to measure both total gold and GRG recovery.
- For low unit recoveries or when size-by-size performance is sought, sample concentrate and tailing streams as well as measure yield.
- For optimizing continuous units, a measure of recovery vs. yield is the most useful information.

Mass balancing can be effected across units, such as jigs, that have a relatively longer residence time, especially for the concentrate fractions as they make their way through the bed. If rapid fluctuations are seen in the plant feed grade then this will result in the deviation in the mass balance, which can be minimized by sampling over a few (3–5) average retention times.

In order to accurately measure the mass flow in those streams typified by higher flow rates it is best to utilize a magnetic flow meter. These units allow for very accurate measurement of flows in a pipeline. Mass flow loops incorporating nucleonic density meters and flow meters can be used to measure both flow and density but are very seldom utilized in gravity circuits due to cost.

Manual flow measurement (*i.e.* using a large container to collect the full stream over a measured time) is cumbersome but in some cases necessary to estimate yield reliably. This applies both to continuous and semi-continuous units. For continuous units, the concentrate stream can often be measured manually, as the flow is generally relatively low. For semi-continuous units, the full concentrate should be recovered, dried, weighed and sub-sampled. Feed flow estimates may be more difficult to obtain. Mass balancing of grinding circuit (*i.e.* size distribution of cyclone feed streams, overflow and underflow) may be necessary to estimate circulating loads, from which feed rates can be calculated. Another approach is to establish a water balance at a node that incorporates the addition of a known flowrate of pure water. This is particularly appropriate for gravity units, which routinely use the addition of fluidization water to improve selectivity (*e.g.* jigs and most semi-continuous centrifuge units).

The higher the grade of the sample, the higher the accuracy of the sample assay. The concentrates of semi-continuous units can be directly screened and size fractions assayed with little or no nugget effects. All other streams have a much lower gold content and a significant proportion of the gold is not gravity recoverable. To address both issues, the protocol developed at McGill University consists of collecting a sample such that a sub-sample of 8–12 kg of the minus 850 μm fraction can be processed with a laboratory separator. Virtually all of the GRG, which is responsible for the nugget effect, is recovered into a concentrate mass that is fully assayed on a size-by-size basis.

A 600 g sub-sample of the tailing product is also screened and fractions up to 30 g in weight is assayed. This procedure virtually eliminates the nugget effect, at least at finer particle size, and provides size-by-size total gold and GRG content. The non-GRG content is calculated by difference.

From the above discussion it is clear that if only two streams are sampled to establish a mass balance, one should be the concentrate. Ideally, the second stream should be the tailing, particularly if unit recovery is high. If unit recovery is low, reliable recovery data cannot be obtained if yield is not measured, even when the feed, concentrate and tailing streams are sampled.

As the focus in new developments shifts from GRG recovery to gold carrier recovery, sampling protocols will be modified, and in some cases, simplified, as sulfide concentrations are much higher than that of gold, and much less prone to nugget effects.

6. CONCLUSIONS AND FUTURE TRENDS

The introduction of the Knelson Centrifugal Concentrator in the early to mid-1980s started a trend to more compact, simplified and lower-maintenance circuits. The use of centrifugal concentrators has resulted in increases in fine GRG reporting to gravity concentrates. Semi-continuous centrifugal concentrators recovering GRG make up the bulk of gravity circuits today but with a heavy focus being turned to the more complex sulfide-associated (gold carriers) and hence, to the continuous concentrate recovery devices such as the InLine Pressure Jig, Falcon C and the Kelsey Jig.

The past five years have seen another significant development with batch and continuous intensive cyanidation. The first natural application, still the most common, is for the recovery of GRG typically produced at very low yield by semi-continuous centrifuge units, using the two batch-intensive-cyanidation systems. Continuous intensive cyanidation can treat increasingly high yields, which offers the option of upgrading simpler ores by gravity to achieve lower operating costs at slightly lower recovery, or achieving significantly higher recoveries of complex ores by preferential treatment of gold carriers. In either case the use of intensive cyanidation for a relatively small proportion of the ore lessens the overall environmental impact, and will be a growing trend.

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Chapter 14

Flotation of gold and gold-bearing ores

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1. BACKGROUND

The application of flotation on a reasonable scale within the gold-mining industry commenced in the early 1930s following the introduction of water-soluble flotation collectors (specifically xanthates and dithiophosphate collectors) that allowed differential flotation of sulfide minerals (Weinig and Carpenter, 1937; Rabone, 1939; Richards and Locke, 1940; Taggart, 1945). Prior to that time, a few gold mines in Canada, Australia and Korea built flotation plants as the first step in the treatment of complex and refractory gold ores (Richart, 1912, Taggart, 1927). Flotation collectors on these plants were oils (Hoover, 1916; Taggart, 1927) that generated bulk low-grade gold concentrates, which were difficult to filter and dry. Pre- and post-Second World War and up until late 1960s, most of the flotation activity in the gold industry took place in Canada (Carter, 1957). During this period, Canada was recognized as the second largest gold producer and a sizeable amount of the gold production came from the treatment by flotation of copper–gold ores, refractory gold ores and complex gold ores.

The demand for sulfuric acid initiated by the booming uranium industry during the late 1960s provided the catalyst for the installation of pyrite flotation plants on numerous gold mines in South Africa (Bushell, 1970; Broekman *et al.*, 1987). After roasting the pyrite flotation concentrate to generate sulfur dioxide for the sulfuric acid plant, the remaining calcine was cyanide leached to remove additional liberated gold. The worldwide gold

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boom in the 1980s and 1990s created new opportunities in Australasia (Woodcock and Hamilton, 1993, Africa (Broekman *et al.*, 1987) and the Americas for the exploitation of medium-sized refractory gold deposits by flotation and further treatment of the concentrates by bacterial and pressure leaching. Many copper flotation plants around the world, and particularly those in the Americas, have enough gold in the ore to ensure that special attention is given to maximize the recovery of gold into the copper concentrate. A comprehensive list of these operations, with details of the flotation reagent regimes and circuit configurations that were in existence during the 1980s, is provided by Bassarear (1985). Since that time there has been a significant increase in the availability of selective flotation collectors for gold (Nagaraj, 1997) and these are now widely in use on many large and new copper flotation plants around the world (Damjanovic and Goode, 2000; Winckers, 2002).

1.1. Mineralogy

Gold occurs in a number of minerals (Harris, 1990) and the most important of these is metallic gold and the gold metal alloys (Chryssoulis and Cabri, 1990). Gold tellurides and gold–silver tellurides are of less importance, although in particular deposits, they can account for a significant proportion of the gold content. Aurostibite [$AuSb_2$] and maldonite [Au_2Bi] are rare minerals but are present in some gold deposits. Aurocupride [AuCu] is found in some primary copper ores (Bulatovic, 1997).

Gold particles in an ore deposit will vary in size from large nuggets to particles locked in the crystal lattice of sulfide minerals. These sulfide minerals are referred to as *gold carrier* minerals and contain trace to minor amounts of gold (Taggart, 1927; Chryssoulis and Cabri, 1990). Often it is found that gold ores are refractory due to the small size of the gold particles in the sulfides and concentration by flotation is required, followed either by roasting, bacterial leaching or pressure leaching to liberate the gold prior to cyanidation.

A more detailed treatment of the mineralogical effect on flotation response may be found in Chapter 2.

1.2. General aspects of gold flotation

Most of the reported fundamental work on the flotation of gold has been conducted using high-purity gold and gold–silver alloys with the purpose of determining collector–gold interactions and the nature of adsorption of collector ions or molecules onto the gold surface. In addition, some work has been conducted to decide whether or not pure gold has a natural hydrophobicity and hence some degree of natural floatability. Flotation research work has been conducted on naturally occurring native gold particles recovered from placer deposits and on gold particles selected from lode deposits. The flotation characteristics of gold or gold minerals found in refractory sulfide and copper ores have not been described in detail in the literature. The sparse distribution of discrete gold minerals and particles, as well as their exceedingly low concentration in ores, are the principal reasons for the lack of fundamental work on gold flotation. A great deal of work has been reported on specific ores, but such studies rarely distinguish between the flotation of native gold and other gold minerals. Flotation of gold ores covers a broad field and it is a rather difficult subject to generalize on. Most problems in gold ore flotation are not connected with floating metallic gold. The flotation recovery of free gold (throughout the text *free gold* is synonymous with *liberated gold*) is largely affected by physical constraints such as the shape and size of the gold particles and the stability of the froth. It is a generally accepted fact that liberated gold finer than about 150 μm floats readily with most collectors and in particular xanthates and dithiophosphates. When free gold is floated with other sulfide minerals the extent of bubble loading of sulfide particles may provide a barrier towards the attachment of free gold, thereby reducing flotation performance. Research investigations have until recently typically focused on the individual flotation behaviour of each gold-bearing mineral in synthetic mixtures and not on mixtures of sulfide minerals in 'real' ores (Teague *et al.*, 1999a).

In the flotation process, the main chemical effects are reagent type and pulp pH. Recently, there has been a need to operate circuits at moderate pH levels, to improve separation efficiencies when treating complex low-grade ores, to reduce costs of reagents, to develop reagents that are stable over a wide pH range and to take advantage of the synergistic benefit of mixture collector systems. This has led to ever-increasing research to develop new collectors and mixtures for the flotation of gold-bearing ores (Nagaraj, 1994; Nagaraj, 1997).

1.3. Surface characteristics of pure gold

Several research papers have dealt with the hydrophilic and hydrophobic nature of pure metallic gold and whether either a zero or a finite contact angle is observed (Gardner and Woods, 1977). Some workers measured contact angles on gold; while others did not. The discrepancy between the findings of zero and of high contact angles on a pure gold surface appeared to be due to both the presence of residual polishing agents and organic contaminants (Gardner and Woods, 1977). It is now generally accepted that the surface of pure clean gold is hydrophilic (Tennyson, 1980) and displays a zero contact angle. The hydrophilicity of gold is due to the high Hamaker constant (Drzimala, 1994) and is a result of the strong dispersion attraction forces for water.

2. COLLECTORLESS FLOTATION OF NATURALLY OCCURRING GOLD

Numerous references are to be found in the literature on the observed *skin flotation* of gold, especially during the recovery of gold by gravity separation (Hoover, 1916; Rickard, 1917; Taggart, 1945). On this evidence gold was presumed to be naturally hydrophobic. As discussed above, naturally occurring native gold surfaces are usually found to be hydrophobic; this is a result of the contamination of the gold surface by organic compounds (Wang and Poling, 1983). Untarnished gold of the appropriate particle size has been found to readily float with only a frother (Wang and Poling, 1983; Aksoy and Yarar, 1989). The earliest recorded laboratory work on gold flotation found that gold floated in the presence of frother only, but not if its particle size was too large or if reagents such as calcium oxide or sodium sulfide were added to the pulp (Leaver and Woolf, 1932). Gold can also be rendered hydrophobic by the deposition of sulfur on the surface (Walker *et al.*, 1984).

3. COLLECTORS IN GOLD FLOTATION

3.1. Collector flotation of naturally occurring, placer and liberated gold

Gold hydrophobicity is enhanced by the addition of flotation collectors and no flotation plant relies solely on the natural floatability of gold for its recovery. Naturally occurring or free (liberated) gold is optimally recovered in a flotation circuit at natural or near-natural pulp pH values and with the addition of small amounts of collector. Inherently, naturally floating minerals float fast kinetically (Klimpel, 1999). Flotation tests on placer gold (Wang and Poling, 1983; Aksoy and Yarar, 1989) showed that fine placer gold typically floated readily with common sulfhydryl collectors and common frothers at natural pH without the addition of any special regulating reagents. Gold flotation recoveries ranged from 78 to 99%.

3.2. Flotation collectors for gold and gold carriers

Flotation with *xanthate* collectors involves the anodic oxidation of the collector that may involve sub-processes such as metal xanthate formation, chemisorption of the xanthate ion and oxidation of the xanthate to form dixanthogen (Groot, 1987; Monte *et al.*, 1997). These adsorb onto mineral surfaces, rendering the mineral hydrophobic. It is generally accepted that the xanthate species responsible for the flotation of free gold is dixanthogen (Miller *et al.*, 1986). This is a neutral oil that will adsorb onto the surface of any naturally hydrophobic solid, rendering it floatable (Gardner and Woods, 1974). Dixanthogen may form on gold by either the application of an applied potential or by a mixed potential mechanism in a pulp that involves the reduction of oxygen. Studies have shown that the development of a finite contact angle and the onset of flotation of gold particles occur at a potential close to that of dixanthogen formation (Woods *et al.*, 1994). The longer-chain xanthates are more readily oxidized, generating dixanthogen at lower potentials (Gardner and Woods, 1974). An increase in thiol chain length increases the maximum contact angle, thereby increasing the hydrophobicity of the surface species. Both these attributes favour the use of longer chain xanthates, such as potassium amyl xanthate (PAX) for the flotation of free gold.

It is quite common to encounter silver and other precious metals forming alloys with native gold. The positive effect that silver has on gold floatability was first recognized in experiments using plates of pure gold, silver and gold–silver alloys. The adsorption of ethyl xanthate on silver is generally thought to take place through an electrochemical mechanism of metal xanthate formation on the surfaces (Talonen *et al.*, 1991; Woods *et al.*, 1992; Yoon and Basilio, 1993). For ethyl xanthate, the presence of silver in gold leads to silver xanthate formation at a potential proportionately lower than for dixanthogen formation on pure gold (Leppinen *et al.*, 1991). As a consequence, the flotation of gold–silver alloys can be achieved at potentials considerably lower than that for gold. Xanthate ions chemisorb on silver at potentials below the region at which silver xanthate deposits (Woods *et al.*, 1992). Chemisorbed ethyl xanthate results in finite contact angles on silver surfaces and the initiation of flotation appears to result from the chemisorption process. For more rapid flotation dixanthogen may play a supporting role. The chemisorbed sub-monolayer (Woods *et.al.*, 1995) could be important in retaining the dixanthogen at the gold surface through hydrophobic interactions between the adsorbate and the bulk phase (Woods *et al.*, 1994).

The xanthogen formates are produced by reacting alkyl chloroformate with xanthate salts. They are stable in acidic conditions unlike the xanthates from which they are formed and are stable in the pH range of 5–10.5. The formates appear to have superior pyrite rejection properties compared to xanthates and dithiophoshate (Ackerman *et al.*, 2000).

Dithiophosphates (Nagaraj, 1997; Allan and Woodcock, 2001) are useful secondary collectors (sometimes referred to as *promotors*) to xanthates in gold flotation. It has been known for a long while that Aeropromotor 208 is an effective promoter in gold flotation (Leaver and Woolf, 1934a; Rabone, 1939). Dithiophosphorous acids are known also to adsorb on gold under certain conditions but they are usually considered not to be selective for gold. The monothiophosphates provide a good selectivity for gold values with a high silver content (Nagaraj *et al.*, 1991) and are able to recover gold selectively from some sulfide ores. Silver has been shown to assist adsorption of discresyl monothiophosphate onto gold (Nagaraj *et al.*, 1991; Basilio *et al.*, 1992a). The monothiophosphates are more stable and stronger than xanthates, dithiophosphates and xanthogen formates. They have also found application for selective gold flotation from primary gold ores or for improving gold recovery in base-metal sulfide flotation in alkaline circuits. Monothiophosphates are now used widely on copper–gold flotation plants.

Mercaptobenzothiazole (MBT, Aeropromoter 404) is a fairly specialized collector (Finkelstein and Poling, 1977) and is the preferred collector for the flotation of gold and gold-carrying pyrite in acid circuits (O'Connor and Dunne, 1991). It is also recommended for oxidized and partially oxidized pyritic gold ores. MBT exists mainly in the non-ionized form in acid and alkaline solutions and both forms are more stable than the corresponding forms of xanthate.

The *phosphine-based* collector (Aerophine 3418A) has found application in flotation of silver and silver sulfides (Mingione, 1990). It is also a useful secondary collector in the treatment of copper–gold ores and the addition is characterized by a heavily mineralized froth and fast flotation kinetics. The dicresyl monothiophosphinate and the diisobutyl monothiophosphinate have been found to increase gold recovery significantly from either primary gold ores or gold-containing tailings when used in combination with standard thiol collectors. In the presence of silver, adsorption of the di- and monothiophosphinate was demonstrated by the formation of the corresponding silver complexes (Basilio *et al.*, 1992b).

The *ethoxycarbonyl thiourea* collectors were introduced in the late 1980s (Nagaraj and Avontins, 1988). These collectors were developed as selective collectors for operation at reduced pH values.

The *hexyl ethoxycarbonyl thionocarbamate* collectors, introduced in 1991, have gained commercial acceptance in the industry. They are more selective against iron sulfides than the simple dialkyl thionocarbamates, even at pH values less than 10, thus affording substantial lime savings. During a plant trial on a European copper–gold ore, an improved gold recovery of 3% was achieved with the modified thionocarbamate (Nagaraj and Avontins, 1988).

Klimpel and Isherwood (1993) described a new family of *electrochemical* flotation collectors that are effective gold collectors with optimum values in the pH range 6–8. These collectors are selective against pyrite at pH values below 10 and afford savings in lime and improved gold recovery when treating copper–gold ores with reasonable contents of pyrite (Dunne, 1991).

Amine-based collectors have been used to float gold and gold-bearing pyrite (Levin and Veitch, 1970). The application is limited as the amine collector is selective for pyrite at high pH values (>10) only. Industrial-scale application of amine collectors are recorded at Venterpost Gold mine in South Africa (O'Connor and Dunne, 1991) and at the Kerr Addison Mine in Canada where the sand fraction from the deslimed cyanide-leach tailing was floated and the concentrate was roasted (Ramsay, 1978).

Table 1
List of specific and blended collectors used for gold flotation

Collector composition – individual collectors	Cytec reagent details
Sodium *iso*butyl xanthate	AERO 317
Potassium amyl xanthate	AERO 343
Xanthogen formate formulation	AERO 3758
*Diiso*butyl *di*thiophosphate	AERO 3477
Mercaptobenzothiazole	AERO 404
*Mono*thiophosphate	AERO 6697
*Di*thiophosphate formulation	Reagent S-9810
Collector composition – blended collectors	
*Di*thiophosphate/*mono*thiophosphate formulation	AERO 7249
*Mono*thiophosphate/*di*thiophosphate formulation	AERO 8761
*Di*thiophosphate/*mono*thiophosphate/*di*thiophosphinate formulation	Reagent S-9913
*Di*thiophosphate/mercaptobenzothiazole formulation	AERO 405
*Di*thiophosphate/mercaptobenzothiazole formulation	AERO 7156
Thionocarbamate/*di*thiophosphate formulation	AERO 3926
Thionocarbamate/*di*thiophosphate formulation	AERO 473
Modified thionocarbamate/*di*thiophosphate formulations	AERO 5744/5
*Di*cresyl *di*thiophosphate formulation	Reagent S-8985
Modified thionocarbamate/*di*thiophosphate/*mono*thiophosphate formulation	Reagent S-9889
Ethyl octyl sulfide formulation	Reagent S-701
*Di*thiocarbamate/sodium hydrosulfide formulation	Reagent S-3730

Very few gold flotation plants use single collectors and the preference is either to add a *blended* collector, that is, a mixture of a number of collectors, or collectors added separately in smaller quantities than those of the primary collector. These collector combinations result in better overall flotation recoveries. The term *synergism* is often applied to this phenomenon. The order of addition of the different collectors can also be important in improving flotation performance (O'Connor *et al.*, 1990). Dithiophosphates are probably the most widely used promoters in gold flotation (Pickett, 1978; O'Connor and Dunne, 1991). A list of the more common collectors and blends of collectors that are presently in use on gold flotation plants is tabulated in Table 1. The Cytec equivalent collector (Cytec Industries Inc., 2002) is also provided.

4. FROTHERS IN GOLD FLOTATION

The strength and stability of the froth is important when floating free gold. There appears to be a preference for polyglycol ether-based frothers on most gold plants in combination with one or other frothers. When selectivity is required or, in the case of copper–gold ores, where a copper concentrate is sold to a smelter, a weaker frother such as methyl isobutyl carbinol (MIBC) is preferred. The choice of a particle size-balanced frother is also an important consideration in gold flotation as this promotes composite particle recovery in the scavenger flotation circuit. As a rule, the glycol or polypropylene glycol methyl ether frothers are ideal for this application (Klimpel, 1997). The blended interfroth frothers have found wide acceptance on Australian gold plants and the base reagent is an alkyl aryl ester (Goold, 1990).

5. ACTIVATORS IN GOLD FLOTATION

Activation implies improved floatability of a mineral after the addition of a soluble base metal salt or sulfidizer. It is generally thought that the metal or sulfide ion adsorbs onto the mineral surface thus changing its surface chemical properties. In this way, the flotation response can be improved and/or the pH range of flotation for the mineral can be extended, the rates of flotation increased and selectivity improved.

5.1. Metal salts

Early work on gold particles with copper sulfate showed no improvement in recovery but an increased rate of flotation of gold (Leaver and Woolf, 1934). More recent laboratory testwork on a refractory gold ore has shown, however, that a 5% increase in free gold flotation recovery is achievable when adding copper sulfate (Teague *et al.*, 1999b). The reason for improved flotation recovery and rate is not understood as the mechanism of surface activation, if it exists, is different from that for sulfide minerals (Allan and Woodcock, 2001).

It is widely accepted that the main purpose of copper sulfate in the flotation of sulfide gold carriers is to enhance the flotation of the sulfides and, in particular, pyrrhotite (Mitrofanov and Kushnikova, 1959), arsenopyrite (Gegg, 1949; O'Connor *et al.*, 1990) and pyrite (Bushell and Krauss, 1962). The sequence of copper sulfate addition (before or after the collector) is important. For arsenopyrite and pyrrhotite, the preference is for copper sulfate to be added first (Teague *et al.*, 1999b; Monte *et al.*, 2002) and recovery differentials as large as 20% are apparent when this is done (Teague *et al.*, 1999b). The addition of copper sulfate has been found to increase the rate of pyrite flotation, providing an overall increase in gold recovery because of the gold association with pyrite (Allison *et al.*, 1982; Duchen and Carter, 1986). In this application, the activation with copper sulfate enhanced the flotation of coarse pyrite. The adsorption of copper onto pyrite and pyrrhotite is pH-dependent, smaller quantities being adsorbed at alkaline conditions. For some ores, the addition of copper sulfate at intermediate pH values such as 7–10 may be harmful and may reduce pyrite recovery (Bushell, 1970).

The activation of the mineral surface by adsorption of copper ions to allow the enhanced adsorption of collector has been touted as one mechanism that provides the improved flotation performance (Leppinen, 1990; Leppinen *et al.*, 1995; Nagaraj, 1997; Nagaraj and Brinen, 1995). The redox potential of the pulp will also increase with the addition of copper sulfate, thereby increasing the oxidizing environment for thiol collectors, thus favouring improved flotation performance (Nicol, 1984).

In some situations, copper sulfate is classified as a froth modifier (O'Connor and Dunne, 1991). As an example, when floating pyrite, it was found that when copper sulfate was not added or added prior to or after the collector, then the froth contained a high proportion of slime and lower grades of concentrates were produced (Allison and Dunne, 1985). In recent laboratory testwork on a pyritic gold-ore, the effect of copper sulfate addition was to increase the concentrate mass and water recoveries (Bradshaw, 1997). This was accompanied by a significant decrease in concentrate grade. This effect did not enhance the overall metallurgical performance as the sulfur grade vs. recovery relationship did not increase, but the froth characteristics were affected. A survey of plant operations (O'Connor and Dunne, 1991) revealed that many flotation operators observe that copper sulfate addition appears to influence mainly the froth stability and that there is an optimum dosage – too little resulting in high slime recoveries and too much resulting in froth instability (O'Connor *et al.*, 1990).

Too high an addition of copper sulfate is known to have negative effect on flotation recovery (O'Connor *et al.*, 1990; Bulatovic, 1997; Yan and Hariyasa, 1997; Monte *et al.*, 2002). Copper is known to be an oxidant for xanthate, so when it is added to the pulp, it will oxidize greater amounts of xanthate to dixanthogen in solution, and this could be the reason for the sulfide and gold depression instead of being activated (Finkelstein and Poling, 1997; Teague *et al.*, 2000). It is claimed that copper activation is incompatible with simultaneous high free-gold and sulfide flotation recoveries.

On some gold mines where flotation was carried out after cyanide leaching, it was normal practice first to condition the pulp at a low pH value of 3–5 and during this period add copper sulfate (Broekman *et al.*, 1987). The conditioning times and amounts of copper sulfate added varied depending on the pH value (Clay and Rabone, 1951; Lloyd, 1981; Botelho de Sousa and Ross, 1990). It is said that the copper sulfate is added to complex the cyanide, decreasing its harmful influence.

Lead nitrate or acetate is often used for the activation of stibnite in preference to copper sulfate (Oberbilling, 1964). The reason appears to be price related, lead salts being cheaper, as copper sulfate has been shown to be the superior activator for many stibnite ores. At the Three Mile Hill Gold Mine in Western Australia, lead nitrate was added as an activator to assist in the preferential flotation of arsenopyrite from pyrrhotite (Bax and Bax, 1993), while lead acetate was used at the Surcease Mine in California to produce a bulk sulfide concentrate for roasting (Jones, 1940). The recommended activator to float arsenopyrite in the nitrogen-based N_2TEC process is lead nitrate (Simmons *et al.*, 1999). Lead activation of pyrite, covellite and chalcopyrite has also been studied (Sutherland and Wark, 1955).

5.2. Sulfidization

The application of *sulfidizers* (sodium sulfide and sodium hydrosulfide) to enhance the flotation of oxidized ores is well known (Jones and Woodcock, 1984; Oudenne and de Cuyper, 1986; O'Connor and Dunne, 1991). The first detailed laboratory study of the influence of sodium sulfide on the flotation of gold-bearing ores was undertaken in the mid 1930s (Leaver and Woolf, 1935). The outcome from this study was that, in general, sodium sulfide retards the flotation of gold, although for some ores there was benefit in its addition. Similar comments are to be found in the literature since that time (Taggart, 1945; Aksoy and Yarar, 1989). Sulfide ions appear to act as flotation activators at low concentrations (less than 10^{-5} M) and as a strong depressant at concentrations above 10^{-5} M (Aksoy and Yarar, 1989). The addition of sulfide ions converts some coatings on mineral surfaces in sulfides (Healy, 1984) and subsequent xanthate addition will promote flotation. For successful activation, the sulfide activator should be added slowly and at starvation quantities.

A recent study of a number of flotation plants found that floated gold grains in the concentrate had a greater concentration of silver and sulfur than the gold remaining in the tailings, implying that they assisted gold flotation (Chryssoulis, 2001). Laboratory flotation tests on a flotation-plant tailing sample using NaHS and Silver ions recovered 30–45% of the unfloated gold and NaSH provided the best results. Application of this information at plant scale resulted in a 7% increase in gold recovery at the Los Pelambres Mine in Chile (Chryssoulis, 2001). Rejected gold particles at this mine were found to be coated with lead carbonate.

A recent innovation, the *Controlled Potential Sulfidization* (CPS) process, where the pulp potential is controlled (Jones and Woodcock, 1984; Jones *et al.*, 1986) has been successfully applied at a number of copper–gold ore flotation plants in Australia (Engelhardt, 1990; Lewis, 1990). In this process, sodium sulfide or sodium hydrogen sulfide is added and the solution potential is controlled at about −450 mV prior to flotation.

6. DEPRESSION OF GOLD IN FLOTATION

Depressants for native gold that are usually introduced during the flotation process include compounds such as calcium ions, chloride ions, calcium carbonate, cyanide, sodium silicate, sodium sulfite, ferric and heavy metal ions, tannin and related compounds, starch and other organic depressants and many others (Taggart, 1945; Broekman *et al.*, 1987; Marsden and House, 1992; Lins and Adamian, 1993; Allan and Woodcock, 2001; Chryssoulis, 2001). All of these may competitively adsorb on the gold surface thus preventing the adsorption of the collector(s) added. It has also been suggested that the ferric ions, which would be in the form of hydrated oxides, may act as a physical barrier between the air bubble and gold surface but this effect is reversed simply by washing with water (Aksoy and Yarar, 1989). However, flotation of native gold often proceeds satisfactorily in the presence of many of these compounds. In general, the results reported by different authors are not in good agreement (Allan and Woodcock, 2001). It is likely that other components in solution or on the surface of the gold that were not measured, provide the answer for the different outcomes.

Lime cannot be considered as just a pH modifier and studies have shown that calcium is strongly adsorbed on sulfide minerals and gold at pH values at and above 10 (Healy, 1984; Chryssoulis, 2001). This adsorption is enhanced if excess sulfate in the pulp promotes calcium-sulfate coatings on particles. Desorption of calcium from the surface by reducing the pH can be assisted by the use of specific calcium-complexing ions such as polyphosphate. Furthermore, if the calcium release is attempted while adding excess activator, then a hydrophilic hydroxide coating can result (Healy, 1985). Metals ions introduced from the circuit water, or from soluble metal ions in the ore, may adsorb and nucleate as hydroxide coatings on all particle surfaces, thus inhibiting collector adsorption. The recommended method of flotation treatment (Healy, 1985) is to operate at as low a pH value as practical, avoid rapid increases in pH, add activator slowly or condition separately and keep the tailings dam at a pH of minimum solubility (*i.e.*, maximum metal hydroxide precipitation).

6.1. Selective depression of sulfide minerals

Differential flotation of the iron sulfides (Poling and Beattie, 1984), pyrite, pyrrhotite and arsenopyrite is a unique process in the gold industry. There is scope on some gold mines for differential flotation of pyrite from arsenopyrite or *vice versa* (Draskic *et al.*, 1984; Beattie *et al.*, 1992; Kogan *et al.*, 1986). This is due to the fact that gold in the pyrite portion is usually nonrefractory, the gold being particulate and liberated on finer grinding, while gold in the arsenopyrite is finely disseminated or in *solid solution*. For a short period during 1987 and 1988 a differential flotation circuit separating pyrite from arsenopyrite was in operation at the Harbour Lights Mine in Australia. This involved the selective depression of arsenopyrite from a bulk pyrite–arsenopyrite concentrate with potassium permanganate at a controlled redox potential in the range +400–500 mV (Wong, 2004). The gold-carrying arsenopyrite concentrate was shipped to a basemetal smelter for gold recovery.

The presence of *active* pyrrhotite may cause serious problems in gold cyanidation circuits, resulting in a combination of high cyanide consumption and slow gold leach rates that will affect gold recovery (Bax and Bax, 1993). To overcome these particular problems, a pre-aeration step was included ahead of the flotation circuit at the Three Mile Hill Gold Mine in Western Australia. Pre-aeration of the pulp allowed for the preferential flotation separation of arsenopyrite and pyrite from pyrrhotite. Lead nitrate was added as an activator for arsenopyrite rather than copper sulfate. Flotation separation was more consistent with lead and the presence of lead in the cyanide leach circuit did not impact noticeably on cyanide consumption. The rougher flotation tailing contained low enough gold values to be pumped directly to the tailings dam. The flotation concentrate was finely ground prior to cyanide leaching.

Separation of arsenopyrite [FeAsS] and pyrite [Fe_2S] from stibnite [Sb_2S_3] may be achieved in strongly alkaline conditions with the addition of copper sulfate to float arsenopyrite and pyrite (Zaman, 1985a). After these have been removed, a lead salt is introduced to activate and float the stibnite. Alternatively, all three minerals can be floated simultaneously at lower pH values and then the stibnite is preferentially depressed by increasing the pH value.

6.2. Depression of sulfide minerals with cyanide

The depressing action of cyanide on pyrite during froth flotation is well known and is widely exploited on many flotation plants to selectively separate copper minerals from pyrite. Depression of pyrite by cyanide during froth flotation appears only to take place in solutions containing free cyanide. The depressing action in the presence of cyanide seems to be caused by a decrease in the pyrite surface electrochemical activity, leading to lower collector adsorption (Prestige *et al.*, 1993; De Wet *et al.*, 1997). The depressing effect is reversible and is achieved by diluting the pulp with cyanide-free solution. As an illustration of this washing and repulping effect, a cyanide residue from a gold mine with cyanide-free water was sufficient to negate the depressing effect of the cyanide on the pyrite (Hodgkinson *et al.*, 1994). The most widely used method of reversing the depressing effect of cyanide in the past has been to condition the flotation pulp at pH 3.5–4 with sulfuric acid, or bubbling sulfur dioxide into the slurry, and then add copper sulfate to complex the cyanide and subsequently float the pyrite (Clay and Rabone, 1951; Malloy and Tapper, 1978). Amine collectors are also effective at floating cyanide-depressed pyrite in alkaline solutions, although the flotation rate is slow (Ramsay, 1978; Broekman *et al*., 1987).

7. FLOTATION OF GOLD AND GOLD-BEARING MINERALS

7.1. Differential flotation of natural and liberated gold

Experience has shown that free gold particles can be recovered selectively against pyrite, by keeping the gold particle surfaces as clean as possible of organic species and by removing any adhering slime particles (Klimpel, 1997). This can be achieved with the use of little or no pH regulators, only small dosages of collectors and suitable frother to stabilize the froth, and possibly a small amount of dispersant.

Selectivity for gold against pyrite was found to be enhanced in the presence of collectors such as alkoxy or phenoxy carbonyl alkyl thionocarbamates, dialkyl or diaryl monothiophosphates and monothiophosphinates, glyoxalidine and aminothiophenols (Nagaraj and Avontins, 1988; Marabini *et al*., 1991).

Monothiophosphorous acids have been shown to be able to float gold selectively from base metal sulfides (Nagaraj *et al*., 1991).

The use of hydrogen peroxide as an oxidizing agent in the selective flotation of gold from pyrite with PAX has been demonstrated at laboratory scale (Monte *et al*., 1997). Hydrogen peroxide addition by itself rendered both the gold and pyrite surfaces hydrophobic. The addition of xanthate converted the gold surface into a fairly hydrophobic condition, whereas the pyrite was still hydrophilic at pH values of 10 and higher.

On most flotation plants, there is a tendency to treat sulfide ores containing free gold as though the gold is associated in a massive or complex sulfide mineral matrix. This leads to high dosage levels of collector and activator addition. In this application, xanthate adsorption on both sulfides and gold makes selective flotation rather difficult due to the formation of dixanthogen on both the gold and sulfide surfaces (Woods, 1971; Gardner and Woods, 1977).

7.2. Flotation of telluride minerals

The information available shows that gold tellurides are easily floated and in practice only a frother at a pH value of around 7–9 is required (Smith, 1963; Singh, 1956; Colbert, 1980; Yan and Hariyasa, 1997), while the addition of small amount of copper sulfate may be beneficial. A slightly acid medium is preferred (Smith, 1963). Gold tellurides float well, but recovery is likely to be compromised by the presence of soluble heavy-metal salts (Bulatovic, 1997). The recovery and rate of flotation of telluride minerals is improved by adding a collector such as a xanthate or MBT and individual tellurides will have similar rates of floatability when PAX is the collector (Yan and Hariyasa, 1997).

7.3. Flotation of gold-carrying iron sulfides

Pyrite is known to be oleophilic when the surface is free of oxidation products (Kocabag *et al.*, 1990) but it is nevertheless necessary to use a collector to float pyrite. Thiol collectors are the most commonly used (Poling, 1976; Crozier, 1982; Xiang-Huai and Forssberg, 1991). Pyrite can be recovered optimally in either acidic or alkaline conditions. Xanthates are the primary collectors on the alkaline side and MBT is used when floating in an acidic medium. Blends of different collectors are particularly effective for recovering pyrite and mixtures of xanthate, thiocarbamates and xanthate and xanthate mixed with MBTs have been successfully used. Dithiophosphates are usually used as secondary collectors and on their own are reported to be selective against pyrite and to a lesser extent against arsenopyrite. Amine-based collectors are capable of floating cyanide-leached pyrite without the use of acid pre-conditioning (Levin and Veitch, 1970; Broekman *et al.*, 1987).

Arsenopyrite has very similar properties to pyrite and the flotation conditions for its recovery are similar to pyrite. Arsenopyrite is susceptible to the formation of oxidation products on its surface. Under oxidizing conditions, a high concentration of PAX is required in order to achieve high arsenopyrite recovery (Monte *et al.*, 2002). The reason for this is not clear (Wang and Xie, 1990) but the low rate of arsenopyrite floatability could be attributed to the formation of iron-oxide species on the surface of the arsenopyrite. Oxidation products such as ferric and ferrous ions are also present in the pulp and depending on the chemical conditions these promote the formation of dixanthogen and bulk ferric-xanthate compounds in solution.

Pyrrhotite floats readily in acid and neutral pH ranges (Mitrofanov and Kushnikova, 1959). Surface coatings in the alkaline regions may result in depressed flotation recovery, while collector regimes are similar to those for pyrite flotation (Bushell and Krauss, 1962). Pyrrhotite oxidizes readily and this makes it more difficult to float than arsenopyrite. Oxidation products in solution create flotation problems similar to those mentioned above for arsenopyrite.

The floatability of marcasite appears to be variable as it has been shown to float more readily than pyrite (Taggart, 1945), while more recently, the opposite has been shown (Bulatovic, 1997).

7.4. Flotation of aurostibite, stibnite, and maldonite

No fundamental flotation information is available for the flotation response of aurostibite [$AuSb_2$]; thus its flotation characteristics have been assumed to be similar to those of stibnite. Stibnite [Sb_2S_3] is not an easily floated mineral (Lager and Forssberg, 1989a, b) and activation with a lead or copper salt is normally required to achieve acceptable flotation recovery (Oberbilling, 1964; Davis *et al.*, 1986; Zaman, 1985a). It floats well only in acid or neutral circuits.

Little is known about the flotation response of maldonite [Au_2Bi] and as with aurostibite the flotation response of maldonite is assumed to be similar to those of the bismuth sulfides. The flotation properties of bismuth sulfides are similar to those of base metal sulfides and float well with the usual sulfide collectors (Zaman, 1985b; Glembotskii *et al.*, 1963).

7.5. Flotation of copper–gold ores

For the bulk flotation of copper minerals and gold from supergene copper ores, it is normal practice to add a xanthate as the primary collector and dithiophosphate as a secondary collector (Bulatovic, 1997). This combination gives satisfactory results in respect of copper concentrate grade and copper and gold recoveries. When pyrite is present in the ore, the choice of collectors will generally depend on the ratio of copper to pyrite in the feed. Dithiophosphate collectors are found to be more selective against pyrite and better gold collectors than xanthate (Bulatovic, 1997). With low pyrite contents in the feed, the ultimate gold recovery is dependent on the type of xanthate selected, longer carbon-chain lengths achieving higher gold recovery. Ores containing large amounts of pyrite require collectors that are selective towards both the copper minerals and free gold. For these ores, the preferred collectors are the dithiophosphates and the new generation of ‘gold’ collectors (refer Table 1). Recent laboratory testwork on a copper–gold ore containing pyrite showed that Aerofloat 7249 achieved the highest gold recovery (Forrest *et al.*, 2001). Aerofloat 6697 provided the best gold concentrate grade at pH values less than 11.5 while Aerofloat 7249 and Aerofloat 208 were better at pH values above 11.5 and gold grades in excess of 250 g/t were generated. At industrial scale, the use of Aerofloat 7249 provided a 4.5% improved gold recovery at the Freeport Copper Mine (Hartati *et al.*, 1997), while the addition of 3477 in the cleaner scavenger circuit improved the recovery of tarnished flaky gold at the Kemess Copper–Gold Mine in Canada (Chryssoulis *et al.*, 2003b).

8. INFLUENCE OF CONDITIONS ON GOLD FLOTATION

8.1. Eh of the flotation pulp

Eh has been shown to be a significant parameter in the flotation of precious metals and sulfide minerals (Woods, 1984; Jones and Woodcock, 1984; Hintikka and Leppinen, 1995). The Eh provides a measure of the oxidizing or reducing capacity of the solution phase in a flotation pulp. When a mixture of two or more sulfide minerals is ground in a steel mill, there are galvanic interactions between the minerals and the steel grinding media. Redox reactions that occur cause current flow leading to surface oxidation of the metals and minerals. Minerals and metals with high rest potential (*i.e.*, noble) act as a cathode, while minerals and metals with lower rest potential (active component) act as the anode. The cathodic reaction will consume oxygen and produce hydroxyl ions while the anodic reaction for a sulfide mineral will provide metal cations and elemental sulfur. The generic reactions are shown below:

$$\text{Cathodic reaction}: \tfrac{1}{2}O_2 + H_2O + 2e \rightarrow 2OH^- \quad (1)$$

Anodic reaction:

$$MeS \rightarrow Me^{2+} + S + 2e \quad (2)$$

Overall reaction:

$$MeS + \tfrac{1}{2}O_2 + H_2O \rightarrow Me^{2+} + S + 2OH^- \quad (3)$$

The hydroxyl ions can adsorb onto mineral surfaces or react with metal ions in solution to form hydroxides that precipitate on mineral surfaces. Predicting the Eh in a flotation pulp is complicated by the many galvanic interactions that occur in the system (Rao *et al.*, 1976; Martin *et al.*, 1992). In practice, sulfide flotation plants operate at pulp potentials that are in the range of +50 to +200 mV vs. SHE (Grano, 2004) and the value depends on the pulp pH, type and quantity of sulfide minerals, the type and quantity of grinding media (Rao *et al.*, 1976), and the amount of air–pulp contact in and after the grinding circuit (Teague *et al.*, 1999). The pulp potential in many aerated systems is deemed to be too oxidizing to achieve maximum mineral selectivity by flotation. This is based on the fact that each mineral has a characteristic potential where flotation starts. At too anodic potentials, the potential ranges for individual minerals overlap, causing simultaneous flotation of several minerals and consequently poor selectivity (Ralston, 1991; Chander, 2003). Furthermore, surface oxidation and precipitation of metal hydroxides may be severe enough in certain high-Eh pulps to cause a decrease in flotation performance (Fornasiero and Ralston, 1992).

Eh–pH diagrams are available, and these indicate that the chemisorption of xanthate occurs over a wide range of Eh and pH values (Woods *et al.*, 1992) implying that the flotation of gold can be successfully accomplished over a wide range of conditions. It has been shown under laboratory conditions that the optimum Eh range for native gold flotation (Hintikka and Leppinen, 1995) is between +10 and +60 mV (vs. SCE). Ethyl xanthate has been shown to form dixanthogen on pure gold at potentials above approximately +200 mV (Leppinen *et al.*, 1991). Silver ethyl xanthate is the species formed on pure silver above –30 mV and on a gold–silver alloy of equal gold and silver content at around +20 mV. From this, it is obvious that the flotation of gold–silver alloys can be achieved at potentials considerably lower than those for gold.

Laboratory testwork on mixed-sulfide gold-bearing ores showed that the flotation recovery of iron sulfides was highest at +50 mV and the recovery began to decrease at higher potentials (Hintikka and Leppinen, 1995). For copper-activated pyrite, the optimum Eh at a pH value of 9 was +35 mV (Shuhua *et al.*, 2004). Copper minerals, on the other hand, reached a maximum recovery at values of between +150 and +200 mV (Hintikka and Leppinen, 1995). The recovery of arsenic minerals was found to progressively increase up to +150 mV followed by a slight drop at +200 mV and rapidly decreased at higher potentials. The potential drop of arsenic at +200 mV is explained by the presence of two arsenic minerals löllingite [$FeAs_2$] and arsenopyrite [FeAsS]. Löllingite is predicted to float at a lower potential than arsenopyrite.

8.2. Flotation gases and the impact of oxidation on flotation

The presence of oxygen is a prerequisite for the flotation of sulfide minerals with thiol collectors (Gardner and Woods, 1974). Electrochemical investigations have shown that the role of oxygen is to provide a cathodic reduction process that allows anodic oxidation processes, involving the flotation collector, to occur on the mineral surface. For example, the collector PAX, which is used on many gold flotation plants, is readily soluble in water and dissociates into positively charged potassium ions and negatively charged polar amyl xanthate ions in a pulp. Chemisorption of the xanthate ion onto the mineral surface then occurs and can render some minerals hydrophobic. For some mineral systems, the chemisorption step is followed by electrochemical oxidation of the adsorbed xanthate to give oxidized species (dixanthogen) that render the sulfide surface hydrophobic. Oxygen for the chemical reactions is introduced into flotation pulps by air entrainment in the grinding and classification circuits and during pumping of the pulp. More oxygen is provided during flotation as air is added in the flotation cells to generate bubbles.

Reduced flotation performance may also result from oxidation products of easily oxidized minerals, such as pyrrhotite and arsenopyrite. These oxidation products can attach unselectively on minerals in the pulp, thus enhancing their floatability (Hintikka and Leppinen, 1995). Reduced selectivity can also arise from the formation of elemental sulfur, thiosulfate, metal hydroxides and other surface layers that are frequently detected in aerated mineral slurries (Smart, 1991). In flotation processes where excessive oxidation causes problems, the application of a reducing agent, such as sodium sulfide, is useful to restore the pulp potential to an appropriate level.

The use of nitrogen bubbles instead of oxygen may provide a more controlled environment for flotation (Gardner and Woods, 1974; Martin *et al.*, 1989; Hintikka and Leppinen, 1995). This approach has been demonstrated at laboratory scale (Monte *et al.*, 2002), where a flotation pulp was preconditioned with nitrogen gas to control the potential below −0.1 V, thus inhibiting the formation of oxidation products on the sulfide–mineral surfaces. At industrial scale the nitrogen-based N_2Tec process is being successfully applied at two flotation plants in Nevada, USA to recover gold-carrying arsenian pyrite (Simmons *et al.*, 1999).

8.3. Modification of pH for flotation

An important consideration when selecting the reagent scheme for the flotation of a particular ore is the choice of pH value and pH modifier (Bulatovic, 1997). Lime and sulfuric acid are presently the most common pH modifiers. In the past, soda ash (sodium carbonate) was extensively used in preference to lime for gold flotation (Taggart, 1945). Sodium carbonate is a common additive to precipitate heavy-metal ions and calcium ions while buffering the solution in the pH range 8–9; all of these conditions are favourable for the flotation of free gold (Allan and Woodcock, 2001). The pH value chosen for gold flotation is dependent on a number of factors (Broekman *et al.*, 1987) and the selection usually takes account of the type and quantity of gangue components (both sulfide and silicate) in the ore. Certain clay minerals are very floatable in the pH range 5–9 and if these are present in the ore, then pH values outside this range are chosen for flotation (Bushell, 1970).

The adverse effect of high pH on the flotation of metallic gold when lime is added has been discussed widely in the literature (Leaver and Woolf, 1932; Taggart, 1945). The recent application of surface analytical techniques has provided compelling evidence of the loss of free gold due to depression induced by surface-bound calcium and hydroxyl ions (Chryssoulis, 2001). The benefit to gold recovery by reducing the pH value from 10.5 to 9 has been demonstrated at the Candelaria Copper Mine in Chile, where a 10% increase in gold recovery was realized at the lower slurry pH (Kendrick *et al.*, 2003). In some circumstances, gold has been found to be more floatable than pyrite and more so at high pH values (Allison and Dunne, 1985).

Pyrite and arsenopyrite float well in the pH range 3–10. This excludes the addition of an activator such as copper sulfate. The depression of pyrite at high pH values can be overcome by the addition of more collector, stronger collector and copper sulfate. Pyrrhotite floats best in acid circuits. The pH range for flotation for gold sulfide ores containing pyrite and arsenopyrite is generally between 7 and 9. Flotation may be carried out at higher pH values of 9 to 10, since this favours the depression of talc minerals and avoids the use of expensive gangue depressants.

Copper minerals are floated in alkaline circuits. There is a preference to float at high pH values to depress pyrite if a reasonable amount of pyrite is present or at natural pH value if there is only a small amount of pyrite present.

8.4. Particle size and shape in flotation

It is well known that particle size is an important parameter in flotation and that size limits exist at which minerals will and will not float. The high particle-density of gold and its malleable and ductile properties that favour the propagation of platy particles, further compound this effect. Platy/flaky particles are formed in the treatment process, particularly in grinding, or during transportation events in nature (Rickard, 1917; Askoy and Yarar, 1989). During these events, some gold particles are impregnated with non-floatable particles (Taggart, 1945; Pevzner *et al.*, 1966), inhibiting flotation. Passivation of a gold-particle surface may also occur after considerable hammering by steel grinding-media (Pevzner *et al.*, 1966). On the other hand, it is postulated that the surface of the gold could become more *active* and therefore more floatable due to *work hardening* (Allan and Woodcock, 2001).

It has been suggested that the practical particle size limits for gold flotation are around 5–200 μm (Allan and Woodcock, 2001). Particles as small as 3 μm have been floated at laboratory scale (Allison and Dunne, 1985), while actual measurements indicate that the flotation performance on many gold plants decrease rapidly below 10 μm (Chryssoulis, 2004). At the coarse end, gold particles as large as 300 μm (Leaver and Woolf, 1934b) and 700 μm have been floated in laboratory flotation cells under specific operating conditions and high collector additions (Lins and Adamian, 1993). Flotation of 590 μm gold particles has been reported on an industrial scale with 'unit' flotation cells (Leaver and Woolf, 1934).

Pulp density and aeration rates influence flotation-cell pulp hydrodynamics and are important parameters in extending the particle-size limits of gold flotation. There is conflicting commentary on the best pulp density for gold particle flotation, both a high pulp-density (Leaver and Woolf, 1934a) and a low pulp-density being recommended (Fahrenwald *et al.*, 1936; Lins and Adamian, 1993).

8.5. Flotation kinetics

Gold is reported not to float as readily or as rapidly as most of the mineral sulfides and thus, it is inherently a slow kinetic process (Leaver and Woolf, 1934a; Klimpel, 1997). Conditions that may further aggravate this are an excessive amount of collector; high clay slimes content (Taggart, 1945; Botelho de Sousa *et al.*, 1986), surface coatings, and cold process-water conditions (More and Pawson, 1978; O'Connor *et al.*, 1988). Large free gold particles float more slowly than finer particles. At the Kemess Gold Mine in Canada the 20–100 μm particle-size free gold floated rapidly in the first three rougher cells. The 5–20 μm gold particles floated at a slower rate and interestingly, the coarser gold (> 100 μm) was recovered in the first two rougher and last rougher-scavenger cells (Chryssoulis *et al.*, 2003). Collector addition in stages has been shown to accelerate free gold flotation kinetics and more so for coarse *flaky* particles (Chryssoulis *et al.*, 2003). Another way to achieve a similar outcome is to select a collector depending on the surface composition of the gold. The impact of higher collector addition is more obvious for the harder to float coated (tarnished) gold particles (Chryssoulis and Dimov, 2004). The addition of copper sulfate has been found to increase the rate of gold flotation; however, it may (Teague *et al.*, 2000) or may not (Leaver and Woolf, 1934a) increase the recovery of free gold.

8.6. Electrical double layer

The electrical double layer that forms at the mineral–solution interface is generated by the presence of potential-determining ions in the mineral–solution (pulp) system. The electrical double layer is important because collector, activator and depression adsorption depend on this, as does the attachment of some particles to bubbles. The sign and magnitude of the surface charges on the species in the system are important issues in the flotation system. A high surface charge on a mineral surface will inhibit the chemisorption of a collector. The dispersed and flocculated state of a mineral pulp is also controlled by the electrical double layer.

8.7. Slime coatings and floatable non-sulfide gangue

The deleterious impact of clay slimes on gold flotation is well known (Rickard, 1917; Leaver and Woolf, 1932, 1934a; Richards and Locke, 1940; Orel *et al.*, 1986). The failure of free gold and sulfide minerals to float has at times been shown to be related to the presence of coatings of colloidal or near-colloidal gangue or silicate material adhering to the mineral surface. These coatings are formed under pulp conditions in which the sulfide particles and silicate particles are oppositely charged. Gangue minerals that are known to cause problems include talcose and carbonaceous minerals, bentonite clay, goethite [FeO(OH)] (Leaver and Woolf, 1934), iron oxide and manganese slimes, pyrophyllite [$AlSi_2O_5OH$] (O'Connor and Dunne, 1991) and carbonates (Da Silva *et al.*, 1989). Slime coatings are controlled by the use of gangue-dispersing agents. Sodium silicate is widely used for this purpose and is most effective when the alkalinity is carefully controlled. Sodium sulfide has also been found to be an effective dispersing agent. In addition to coating the mineral surface, the gangue particles may coat the bubble surface, affecting the ability of any gold and sulfide particles to attach to the air bubbles (Allison *et al.*, 1982; Aksoy and Yarar, 1989). Other more recent remedies to overcome the problem of slime coatings have included physical methods such as removal of the slimes by cycloning (Bushell, 1970; Broekman *et al.*, 1987), high-intensity attritioning (Duchen and Carter, 1986; Valderrama and Rubio, 1998; Allan and Woodcock, 2001) and a lower pulp density (Bulatovic, 1997).

Organic compounds of high molecular weight that maintain a state of dispersion of deleterious slime components by forming wettable coatings on the gangue particles are used for much the same purpose as the inorganic dispersing agents. These organic compounds are referred to as organic gangue depressants. Typical examples are glue, starch, dextrin, gum arabic, carboxymethylcellulose and the more recent modified-guar gums.

Selection of the correct depressant type and dosage is critical, as an overdose results in both loss of free gold (Leaver and Woolf, 1934) and sulfides that contain gold (Steenberg, 1984). The anionic polymers (guar gums, cellulose gums, modified lignin sulfonates) generally have a negligible depressant capability on sulfide minerals while the cationic polymers (starches, dextrin, tannin derivatives, oxycellulose) are capable of acting as sulfide-mineral depressants (Bulatovic, 1999). The combination of a collector and depressant is also important since in the flotation of pyrite, for example, guar gum will have a more adverse effect when used with MBT than with xanthate (Steenberg, 1984).

An alternative approach that has had some success is to add small quantities of frother to the pulp and selectively float the talcaceous minerals prior to removing the bulk sulfide concentrate. These talc concentrates may contain up to 30%–40% of the gold contained in the feed and this concentrate can either be cyanide leached separately or recombined with the sulfide tailing prior to cyanidation (O'Connor and Dunne, 1991).

Porphyry copper–gold ores usually contain some gangue components that are highly floatable and contaminate the copper concentrate. Maintenance of a high copper-concentrate grade requires that gangue depressants be used. Silicates, guars and carboxymethylcellulose are the common depressants (Bulatovic, 1997) applied in the copper industry.

Carbonaceous and graphitic minerals are soft and flaky, and easily broken down during grinding. During flotation, the carbon floats readily owing to its fine grain size, natural hydrophobicity, platy nature and low density (Swash, 1988). Graphitic carbon and clays can be the cause of poor gold recovery on many refractory gold or flotation plants (Swash, 1988; Bulatovic, 1997). Carbonaceous-containing gangues have in the past been treated to provide either a gold-free carbon concentrate while depressing the gold and sulfide minerals, or floating the gold and pyrite with the carbonaceous matter being depressed. The former method was used at the McIntyre Porcupine where quebracho was added to depress gold and auriferous pyrite and the carbonaceous component was floated with fuel oil and MIBC (Nice, 1971). At a pyrite flotation plant in South Africa, a dextrin–guar–lignosol reagent acted as the graphite gangue depressant (Allan and Woodcock, 2001) and a gold–pyrite concentrate was floated using Aerofloat 25 and, Dowfroth 250. Active carbon components in gold ores are known to float better when a fuel oil is used in combination with a frother (Ramsay, 1978; Bulatovic, 1997). In the nitrogen-based N_2TEC process, there is likely to be erratic flotation behaviour of the carbonaceous material, if it is present in significant amounts in the feed (Simmons, 1997). Each carbon species requires its own specific reagent and flotation conditions.

8.8. Natural metal and organic coatings on gold

Most coatings on mineral surfaces are detrimental to flotation, but in some cases, the effects can be overcome (Allan and Woodcock, 2001). Many types of surface coatings have been reported to occur on native gold particles. Perhaps the most difficult coatings to cope with are hydrated iron oxides (Richart, 1912; Richards and Locke, 1940; Brooke *et al.*, 2003). The surfaces of gold particles can become coated naturally with precipitates of iron, from oxidized sulfides in an orebody or from rusting iron, such as iron grinding media, as first reported by Head (1936). Gold from placer deposits heavily stained or coated by iron oxides or impregnated by hydrophilic minerals is not easily floated (Wang and Poling, 1983). Tarnished gold has been found also to have a markedly higher mercury content compared to 'shiny' gold (Chryssoulis *et al.*, 2003a). Gold particles coated with manganese dioxide have also been reported (Richards and Locke, 1940).

Some gold flotation pulps may contain humic and tannin substances (organic decay products from wood and vegetation) and sulfide ions from sulfide mineral (Aksoy and Yarar, 1989) that are reported to impact on gold flotation. Humic acid has been found to be only marginally deleterious to gold flotation (Aksoy and Yarar, 1989) and some naturally occurring organic coatings can be removed by conditioning with sodium hydroxide or acid solution (Johns, 1935).

Methods to improve the flotation of gold-coated particles include more collector, acid treatment (Brooke *et al.*, 2003), chelating agents, water wash and organic acids (Bulatovic, 1997). Flotation of some coated particles, even when a high dosage of collector is employed, is reported to be weak and erratic.

9. FLOTATION CIRCUITS

Flotation circuit configuration on most gold mines can be divided into a number of categories, *viz*. open circuits with no cleaning at all, and open and closed circuits with single stage and two stages of cleaning. Open circuits have the advantage of no feedback from the effects of non-steady-state operation and therefore are inherently more stable than the closed-circuit configuration. Closed and open-circuit flotation cleaning is used on gold mines where high-grade concentrates are required for roasting and smelting. Under these conditions, it is difficult to maintain very high gold and sulfide flotation recoveries, while also producing an acceptable grade of concentrate. Where there is no constraint on concentrate quality, high gold and sulfide flotation recoveries are achievable to the extent that a discardable gold flotation tail is possible (Bax and Bax, 1993; O'Connor and Dunne, 1991). Cleaning-circuit configuration, either single or two stages of cleaning, and cleaner residence time are related to the particle size of the sulfides in the flotation feed and also the presence or absence of floatable gangue components.

Unit flotation cells (Hasting, 1937; Taggart, 1945) and the more recent Flash flotation cells (Kalloinen and Tarainen, 1984) are installed in grinding circuits with the purpose of improving the overall flotation recovery of free gold (Taggart, 1945; Suttill, 1990; Laplante and Dunne, 2002). The aim is to remove as much of the free gold contained in the circulating load of the grinding mill before it is *overground* or is covered with coatings of iron, sulfide or other coatings that will lower flotation recoveries. Improved overall gold flotation recoveries of 2–10% have been quoted (Sandstrom and Jonsson, 1988; Jennings and Traczyk, 1988; McCulloch, 1990). Furthermore, the inclusion of Unit and Flash flotation cells will generally provide better flotation stability and performance. Improved overall gold flotation recoveries from 3% to 10% have been quoted (Sandstrom and Jonsson, 1988; Jennings and Traczyk, 1988; McCulloch, 1990) for ores of variable gold and sulfide content (Taggart, 1945).

Column flotation cells are used in roughing and cleaning duties on a number of mines treating gold ores (Lane and Dunne, 1987). A column cell typically provides higher concentrate grades compared to a mechanically agitated cell; however, losses of coarse gold may be higher in the column cell (Chryssoulis *et al*., 2003b).

10. FLOTATION PRACTICE

It is not unusual for gold to be present in several forms in any given ore deposit. A typical example of a mixed gold ore is one having some level of free or native gold occurring with the remainder being associated with various types of sulfide minerals (Teague *et al.*, 1999a). The selection of an optimal flotation reagent scheme is very dependent on the specific mineralogy of the gold ore to be processed (Blaskett and Woodcock, 1953; Elvey and Woodcock, 1985; Woodcock, 1980).

10.1. Refractory gold ores

Successful concentration of gold in refractory sulfide ores is almost exclusively dependent on the association of the gold with the sulfides (Bulatovic, 1997; O'Connor and Dunne, 1994). Refractory gold ores commonly contain free gold, sub-microscopic gold, carbonaceous material, base metals, pyrite, marcasite, arsenopyrite and pyrrhotite (Swash, 1988). Clays and graphitic carbon are the most troublesome accessory components in some of these ores, as far as gold concentration is concerned. Arsenopyrite has very similar properties to pyrite and the flotation conditions for its recovery are similar to pyrite. Arsenopyrite is marginally less hard and more brittle than pyrite and pyrrhotite (Swash, 1988). During milling, the arsenopyrite is therefore subject to more overgrinding than pyrite and pyrrhotite. The difference in the recovery of these minerals is due not only to the difference in the surface chemical properties of the particle but also to the difference in their overall size distribution.

10.2. Arsenopyrite, pyrrhotite and pyrite ores

In Brazil, the application of flotation for gold-bearing ores started in the 1980s (Araujo and Peres, 1995). There are three important Brazilian plants using flotation to process gold ores (Monte *et al.*, 2002). At the São Bento plant, gold and pyrite are floated into a bulk concentrate for further processing by bacterial and pressure leaching. The Morro Velho mine located at Raposos treats graphitic gold ores that contain free gold and gold associated with pyrite. The first stage of flotation to remove free gold and graphite is accomplished with MBT at neutral pH. The remaining gold containing pyrite is floated in a second stage with the addition of dithiophosphate. The two flotation concentrates are combined ahead of roasting.

In North America, four gold mines treat refractory gold ores. At the Lone Tree and Twin Creeks mines in Nevada, USA, the fine-grained arsenian pyrite that contains most of the gold is floated using the nitrogen-based N_2TEC technology (Simmons, 1997). Flotation takes place at neutral or slightly acid pH values with the addition of lead nitrate as activator and xanthate as collector. The Campbell Mine in Ontario (Chang *et al.*, 1983) treats an arsenopyrite–pyrite ore and the flotation concentrate is pressure leached. Flotation reagents consist of copper sulfate as activator, PAX and AF208 as collector and the frother is Dowfroth 250. Flotation is conducted at natural pH (O'Rourke *et al.*, 2000). At the Snip Mine in British Columbia, Canada, the gold ore is floated at natural pH value (8.5) using Aerophine 3418A and a dithiophosphate, the frother is Dowfroth 250. The flotation concentrate is filtered, bagged and sent to a smelter (Bried *et al.*, 2000).

There are six gold mines in the Australasian region that treat refractory gold ores. The largest of these is the Porgera Gold Mine in Papua New Guinea, where a pyrite–arsenopyrite flotation concentrate is pressure leached. Flotation takes place at natural pH values and PAX is the only collector. The frother is a mixture of MIBC and Dowfroth 400. The Macraes Gold Mine in New Zealand floats a bulk arsenopyrite–pyrite–pyrrhotite sulfide flotation concentrate at natural pH value. Flotation reagents include copper sulfate, sodium *iso*butyl xanthate (SIBX) as the primary collector, a dithiophoshate promoter and two frothers, MIBC and Interfroth 60. There are two gold mines in Australia, the Wiluna Gold Mine in Western Australia and the Beaconsfield Mine in Tasmania that use bacterial oxidation to process bulk arsenopyrite–pyrite flotation concentrate prior to cyanide leaching. At the Wiluna mine, the gold ore is floated at a slightly elevated pH of 8.2 using copper sulfate, PAX and Interfroth 50. A Unit flotation cell is included in the milling circuit at the Beaconsfield mine. Copper sulfate is added to the mill while SIBX is distributed to three different locations in the flotation circuit. At the Kanowna Belle Gold Mine in Western Australia, the combined Flash flotation concentrate, first rougher concentrate and rougher–cleaner concentrate that contains pyrite and arsenopyrite is roasted. Flotation is undertaken at natural pH values with the addition of copper sulfate, PAX and a guar gum depressant.

There are three gold mines on the African continent that have flotation plants treating refractory gold ores. The Ashanti Mine in Ghana employs a combination of column and mechanical flotation cells to produce a bulk concentrate for bacterial leaching. The other two mines, the Fairview Gold Mine and the Sheba Gold Mine, both in South Africa, carry out flotation at natural pH values and add SIBX or thiocarbamates as collector. Copper sulfate is also used at the Sheba flotation plant.

In Australia, the trend is to use the stronger and longer-chain xanthate PAX as collector as this appears to give slightly higher recoveries and better concentrate grades. Most flotation plants treating refractory gold ores add only a single collector and this is also the case on most Australian flotation plants.

10.3. Gold ores containing telluride minerals

The Emperor Mine in Fiji that selectively floated telluride minerals in the 1970s and 1980s provides the best example of an integrated telluride-flotation circuit. Lime was added to the grinding circuit to depress the sulfide minerals

(Colbert, 1980). The telluride minerals were removed with the addition of a small amount of polyoxypropylene glycol ether frother at a pH value of 9. The telluride concentrate was cleaned after the addition of a small amount of sodium silicate as a gangue slime depressant and froth modifier. Soda ash addition to the flotation tailings provided a pH value of 9.5 prior to conditioning the slurry with xanthate and Terric 402 frother and then floating a sulfide concentrate. The sulfide concentrate was reground before cleaning and the cleaned concentrate was roasted ahead of the cyanide-leaching circuit. The telluride concentrate was treated in a separate circuit to recover the gold and tellurium.

The two gold mines of note that contain telluride minerals, the Emperor Mine in Fiji and the Kalgoorlie Consolidated Gold Mine in Kalgoorlie, presently float a bulk sulfide–telluride concentrate for roasting. The flotation reagent suites at these two mines are a combination of copper sulfate, xanthate and frother (see also Chapter 39).

10.4. Pyritic gold ores

South Africa still has three reasonably sized operating pyrite flotation plants, compared to the flurry of activity in the 1990s when some 14 pyrite flotation plants were in existence (Bushell, 1970; Broekman *et al.*, 1987; O'Connor and Dunne, 1991). The three flotation plants that are currently in operation are to be found at the Vaal Reefs Gold Mine and at the Chemwes and Ergo residue re-treatment operations. Copper sulfate is used at two plants (Vaal Reefs and Chemwes), while single collectors are added at the Vaal Reefs Mine (Aeropromoter 407) and Chemwes operation (SIBX). A blended thiol collector is used at the Ergo flotation plant. The pH of flotation is near neutral at all the three plants (pH range 7–8.5).

In North America, the Sonora Mine in the Mother Lode district of California found that a combination of xanthate and Aero 5688 promoter with small additions of depressant was the best option for floating the pyrite–gold ores that occasionally contained large amounts of hydrophobic talc (Hansen and Killey, 1990).

The Rio Paracatu Mineração (RPM) Mine, in the Paracatu district in Brazil (Suttill, 1990, Monte *et al.*, 2002) produces a pyrite concentrate with minor amounts of arsenopyrite, which is reground before cyanide leaching (Monte *et al.*, 2002). Reagents are the standard recipe of copper sulfate and xanthate.

At the Royal Oak Mine in Ontario, Canada, the predominantly pyritic gold ore is treated by flotation to produce a concentrate that is reground to 38 μm prior to pre-aeration and cyanide leaching. Flotation reagents are PAX, dithiophosphate and Dowfroth 250 (Bedard *et al.*, 2000).

Flotation reagents at the Stawell Gold Mine in Victoria, Australia, where carbonaceous pyrite–pyrrhotite gold ores with minor quantities of arsenopyrite are floated at a slightly elevated pH value, include copper sulfate, PAX and Terric 407 frother. The concentrate is reground before cyanide leaching.

10.5. Copper–gold ores

Copper–gold ores are significant contributors to the overall world gold production. Flotation is the principal process for pre-concentration of the copper–gold minerals for subsequent smelting treatment. Gold recovery, although important, is not always considered when optimizing the copper circuit. The need to reject gangue and iron sulfides during cleaning of the copper concentrate, invariably leads to losses of gold. The detrimental effects of depressants, which are introduced in the cleaner circuit, can often be overcome by changing the flowsheet and by adding supplementary collectors. In the treatment of copper–gold ores, mixed collector systems appear to be the norm and selective gold promoters are widely in use.

The processing characteristics of copper–gold ores vary from ore to ore and are closely related to the mineralogical composition of the ore. Based on composition, the ores can be classified into porphyry copper–gold ores containing pyrite, porphyry copper–gold ores with negligible pyrite content and altered supergene copper–gold ores. Supergene alteration leading to the formation of oxide and secondary copper minerals is common.

The amount of *free* gold varies among deposits and is typically higher in the supergene ores. The porphyry-type ores frequently includes free-gold recovery circuits, including Flash flotation and gravity concentration, to improve the overall gold recovery (Winckers, 2002). Many of the copper–gold mines that contain economically significant amounts of gold make use of the selective gold-flotation collectors (refer to Table 1). Mines that fall into this category include the Freeport and Batu Hijau Copper Mines in Indonesia, the Ok Tedi Copper Mine in Papua New Guinea, the Cadia Gold Mine, Olympic Dam Copper Mine, North Parkes Copper Mine, Osborne Copper Mine and the soon to be reopened Telfer Gold Mine in Australia. In North America, the Troilus Copper Mine in Canada and in South America, the Alumbrera Copper Mine in Argentina, and the Candelaria Copper and the Escondida Copper Mines in Chile are also users of selective gold collectors. Further detail on the treatment of gold–copper and copper–gold ores can be found in Chapters 32 and 33, respectively.

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Rob Dunne has worked in the minerals industry for 32 years. He graduated from the University of the Witwatersrand in 1971 with a degree in Metallurgical Engineering. He started work at the Loraine Gold Mine where he learnt about and became intrigued with gold–pyrite flotation. In 1974, he joined Mintek and over a number of years developed a group that specialized in flotation. The group was involved with 'trouble shooting' on mine sites and in the process, developed new and improved flowsheets as well as specialized flotation equipment. These included cleaner flowsheet modification in the gold and platinum industry and the development of coarse particle flotation equipment that was used to float coarse copper at the Palabora Copper Mine. He also contributed to the chapter on Flotation in the book *The Extractive Metallurgy of Gold in South Africa*. In 1986, Robert joined the Western Australia School of Mines in Kalgoorlie. During his 3 years there he wrote and co-authored a number of review papers on the application of column flotation and gold flotation plant practice in Australia. In 1989, Robert joined Newmont Australia which later became Newcrest Mining Limited. During his 14 years at Newcrest, he was involved with the implementation of flotation improvements at the Telfer Gold Mine as well as helping with the development of the flotation flowsheet at the large Cadia Gold Copper Mine in New South Wales. Besides this, Robert involved himself with a number of Australian research organizations and universities that were involved with flotation research. In 2001, he was appointed Adjunct Professor at the University of Queensland. In 2003, he joined the Technical Services Division of Newmont Mining in Perth and currently holds the position of Manager of Process Metallurgy.

II.3 *Oxidation of Sulfide Concentrates*

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Mike D. Adams (Editor)

Chapter 15

Pressure oxidation overview

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Compared to pyrometallurgy, hydrometallurgy is a relatively new discipline, with the majority of developments taking place in the last 100 years (Van Weert, 1989). Pressure hydrometallurgy of gold ores and concentrates is even younger, major developments taking place during the 1980s, barely 20 years ago.

In hydrometallurgical processes for the extraction of metal values from ores or secondary materials (*i.e.*, concentrates) there are three basic procedures (Derry, 1972):

- dissolution of a compound and/or metal value from an ore or concentrate into a leach solution;
- purification and/or upgrading of the leach solution, and
- subsequent recovery of values from the purified solution.

Besides the three basic procedures, there are processes in hydrometallurgy that are utilized, for example, as pretreatment steps. Such is the case in the pressure oxidation of refractory gold ores.

Often there are advantages to be gained by operating at temperatures above the normal boiling point of the solution and, therefore, at pressures above atmospheric. In such cases, the term *pressure hydrometallurgy* is used or applied. Within the gold industry the term *pressure oxidation* is synonymous with pressure hydrometallurgy. *Pressure oxidation* refers to the oxidation of sulfides, such as pyrite [FeS_2] and marcasite [FeS_2], at elevated temperature and pressure. Oxidation releases encapsulated gold grains

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from the sulfides and makes the oxidation residue of the ore or concentrate more amenable for gold recovery by cyanidation in a subsequent leaching step. Pressure oxidation of gold ores is therefore a pretreatment leaching step to enhance gold recovery.

In a very broad sense the definition of *hydrometallurgy* is (Tottle, 1985):

> "That branch of metallurgy concerned with the science and art of extraction of metals from their ores by processes involving solution in water".

Although pressure oxidation of gold ores and concentrates does not directly recover gold in a strict sense of the above definition, it is an essential step to enable the gold to be recovered and accordingly is part of hydrometallurgy. Although used extensively in the alumina industry since the beginning of the 20th century, it did not become popular in the base metal industry until the early 1950s, possibly related to aggressive acid conditions requiring more sophisticated materials of construction.

The two major considerations in hydrometallurgical processes are:

- the *extent* to which a reaction can proceed (*thermodynamic* property) and
- the *rate* at which the reaction will proceed (*kinetic* property).

Therefore, to understand pressure oxidation of gold ores, it is important to consider these two aspects in general terms. The former depends on the thermodynamic properties of the chemical system, which determine the overall reaction driving force. The latter, reaction kinetics, depends on a combination of physical, chemical and mass transport factors and can be influenced to some extent by appropriate plant design.

1. INTRODUCTION

1.1. Thermodynamic considerations

There are three laws of thermodynamics (Glasstone and Lewis, 1965):

First Law:	The total energy of a system and its surroundings remains constant.
Second Law:	All natural or spontaneous processes occurring without external aid are thermodynamically irreversible in character. The fact that a process takes place spontaneously means it takes place at a finite rate. Consequently, thermodynamically reversible changes are required to occur infinitesimally slowly.
Third Law:	In its simplest form the third law states that the entropy (randomness) of a perfect crystalline solid of a pure substance is zero at the absolute zero of temperature. This third law is basically an enunciation to overcome a fundamental problem in establishing zero entropy in substances.

In general, two main influences determine the state of an equilibrium system and control the direction and tendency of natural processes to occur (Schaufelberger, 1956). The first is the ordering influence of attractive forces that can be satisfied with a fall in potential energy (enthalpy) of the system to the surroundings. The other is the opposing, disordering influence of the tendency to chaos. At the absolute zero (third law) the first influence is all-important, but with rising temperature the balance shifts in favour of the second influence until, at very high temperatures, the tendency to chaos (or increased entropy) will be supreme. Normal chemical operations have an interplay between these two opposing forces, the examination of which has become an extensive subject.

The thermodynamic function that comprehends all of this is the Gibbs free energy ΔG, which tends to a minimum value at equilibrium. It is concerned only with changes (ΔG) that accompany various processes. The value of $-\Delta G$ measures the tendency of the process to occur. ΔG is a composite function of the two directive influences, the ordering influence of attractive forces (H) and the tendency to increased randomness (S), stated as (Ives, 1964)

$$\Delta G \rightarrow \Delta H - T\Delta S \tag{1}$$

Chemical equilibrium is the point in a chemical reaction at which there is no further change in the relevant ionic and molecular species. The conditions can be described using equilibrium constant (K) as follows (Marsden and House, 1992):

$$w\mathrm{A} + x\mathrm{B} \rightarrow y\mathrm{C} + z\mathrm{D} \tag{2}$$

$$K \rightarrow \{(a_\mathrm{C})^y(a_\mathrm{D})^z\}/\{(a_\mathrm{A})^w(a_\mathrm{B})^x\} \tag{3}$$

where a denotes activity and lowercase letters are stoichiometric values of the reaction.

The greater the value of the equilibrium constant (K), the greater the tendency for products C and D to form. The energy change associated can be expressed by ΔG, and it can be shown that at equilibrium $\Delta G = 0$, where

$$\Delta G \rightarrow \Delta G^\circ + RT \ln K \tag{4}$$

Thermodynamic data are available for 25°C conditions for most species encountered in gold hydrometallurgy. However, various reactions that are commonly encountered in pressure hydrometallurgy and pressure oxidation processes are performed at elevated temperatures for which experimental enthalpy, entropy or free energy values have not yet been determined. Several groups of workers have used extrapolative methods to yield data up to 300°C (Derry, 1972).

There are several techniques for studying chemical reactions and equilibrium at high temperature, such as *Ellingham diagrams* (ΔG°–temperature diagrams) and *Pourbaix diagrams* (Eh–pH diagrams, also called potential–pH diagrams).

1.2. Kinetic considerations

Whether or not a thermodynamically favourable reaction does in fact proceed, is determined by kinetic factors and is an important consideration in the design and economics of all hydrometallurgical processes. The rate of reaction may be limited by the rate of chemical reaction itself or it may be controlled by transport processes (Derry, 1972). In leaching processes there are complicated heterogeneous reactions at the solid–liquid boundaries, and when gaseous reagents are used, as in the use of oxygen in the pressure oxidation of gold ores, the three-phase system is even more complex. In a three-phase leaching system the reactions can proceed by the following steps:

- transfer of the gas to the liquid phase (transport);
- transfer of reactants to the solid–liquid-phase boundary (transport);
- reaction at the solid–liquid-phase boundary (chemical), and
- transfer of products away from the reaction zone (transport).

In the pressure oxidation of sulfidic gold ores and concentrates the above processes can be considered consecutive.

An increase in temperature will in nearly all cases increase the rate of a chemical reaction to a significant extent; for every 10°C rise in temperature the specific rate is increased by a factor of 2 or 3 (Glasstone and Lewis, 1965). One of the most convenient forms of expressing the relationship between temperature and rate of reaction is the *Arrhenius* equation:

$$k = A\mathrm{e}^{-E/RT} \tag{5}$$

where R is the gas constant, E the activation energy, T the temperature (absolute), k the specific rate and A the collision frequency constant.

In the case of chemical control, the rate of reaction increases rapidly with temperature, with activation energies of the order of 50 kJ/mol. Therefore, operating at temperatures above the atmospheric boiling point enables very high rates of reaction to be obtained. However, if the rate of reaction is limited by transport processes, the net effect of temperature is far less, as activation energies are typically of the order of 20 kJ/mol. Transport mechanisms can be enhanced by controlling partial pressure and agitation. From the standpoint of the quantitative consideration of reaction rates they are classified by the order of reaction, *i.e.*, the number of atoms or molecules whose concentrations (or pressures) determine the rate of reaction (*e.g.*, first, second or third order).

Activation energy data for a number of reactions of interest to gold hydrometallurgists are summarized in Table 1 (Marsden and House, 1992).

The majority of reactions in gold hydrometallurgy can be approximated as first-order reactions. A notable exception is pressure oxidation of sulfides, which might be half order.

Kinetic factors are particularly important in the acid pressure oxidation of sulfides, with oxidation products varying according to the temperatures and pH value of the system (Mackiw *et al.*, 1966). This is illustrated in Fig. 1, which shows that although metal sulfides are oxidized completely to sulfates under acidic conditions at temperatures above 175°C, at lower temperatures

Table 1
Activation energy for selected gold processes

Process	E (kJ/mol)	Rate-limiting step
Zinc precipitation of gold	13–16	Mass transport of $Au(CN)_2^-$
Carbon gold adsorption	11–16	Pore diffusion control of $Au(CN)_2^-$
Sulfide oxidation (by O_2)	30–70	Mass transport of O_2 (high temperature) or chemical control

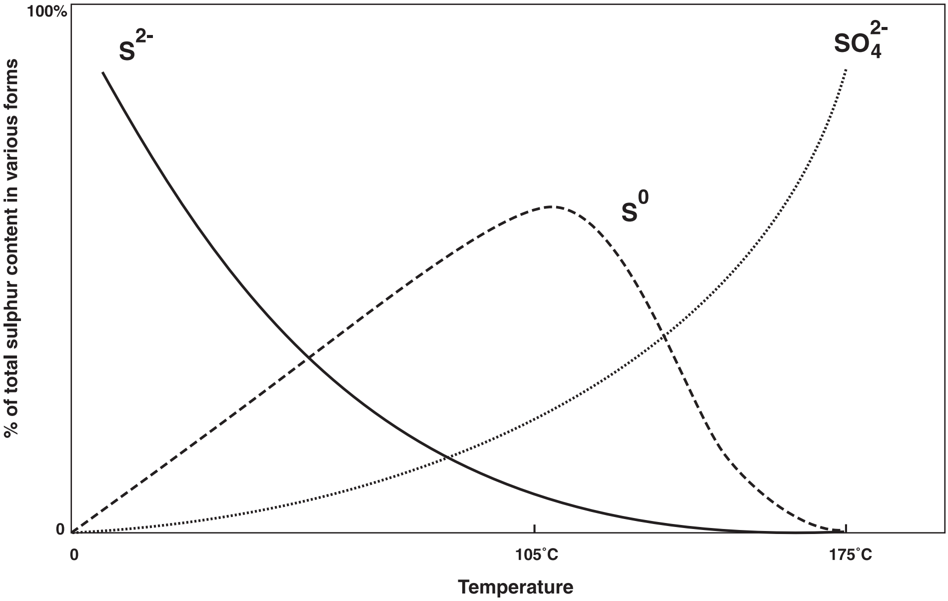

Fig. 1. Oxidation of sulfides at pH values of 3 or less (sulfuric acid–sulfide–oxygen in autoclave) (after Mackiw *et al.*, 1966).

elemental sulfur forms. This pattern of behaviour is particularly important in gold metallurgy involving sulfide ores. The production of elemental sulfur (S° or S_g) is to be avoided as it has the ability to lower gold recovery by absorbing or encapsulating gold in the subsequent gold-cyanidation step. It also has the ability to coat unoxidized sulfide particles, preventing complete oxidation and thereby preventing release of occluded gold. Moreover, it reacts with cyanide during the gold-leaching step, to form thiocyanate, increasing cyanide consumption, and thereby increasing operating costs. Raising the temperature improves the kinetics of oxidation.

1.3. Partial pressure and agitation

The pretreatment leaching step in gold hydrometallurgy involves the use of gaseous oxygen. When gaseous reagents are used in leaching reactions the gas must be transferred to the solution as rapidly as possible. This can be achieved by

- increasing the partial pressure of the gaseous reagent;
- vigorous agitation to increase the surface area of the gas–liquid interface to assist transfer, and
- vigorous agitation to shorten the diffusion path so that the rate-determining step is more likely to be at the solid–liquid reaction boundary.

Vigorous agitation also has a side benefit in solutions containing a high proportion (m/m) of fine solids. Any protective layers formed on the solid surface can be abraded due to the agitation, thereby allowing reaction rates to proceed unimpeded; however, agitation cannot be too vigorous or agitator impellers are worn out prematurely.

The oxidation of sulfides is considered a half- or first-order reaction, and increasing the partial pressure of oxygen increases the reaction rate in addition to the benefit obtained by increasing temperature and agitation.

In pressure-oxidation vessels treating gold ores, practical experience has indicated that the tip speed of axial-type impellers must be kept to a maximum of approximately 4 m/s. Otherwise, accelerated wear of the blades drastically reduces the on-line availability of vessels. Hence, a practical balance must be kept between vigorous agitation and impeller/blade wear. To a certain extent, blade wear can be minimized by improved design as practical experience is gained.

1.4. Environmental considerations

The question may be asked, “why is pressure hydrometallurgy becoming popular?” There are several reasons. Pressure oxidation is in a sense roasting in an aqueous solution in closed vessels, with sulfur and sulfates being formed instead of sulfur dioxide gas. Accordingly, pollution is reduced. For example, in the sulfuric acid processing of zinc concentrates an autoclave is used to convert zinc sulfide concentrate directly into zinc sulfate solution and elemental sulfur, with the subsequent solution purification and electrolysis being the same as used in pyrometallurgical plants. Because elemental sulfur is produced, acid plants and smoke stacks are not required, and air quality and plant working conditions are improved. A similar comparison can be made between roasting and pressure oxidation of gold ores and concentrates. This is especially so for arsenopyrite-bearing gold, where arsenic and sulfide are fixed as ferric arsenate and sulfates, respectively, in pressure oxidation, whereas roasting produces toxic sulfur dioxide gas and arsenic trioxide fumes.

At Placer Dome's Campbell Mine in Northern Ontario, Canada, a gold pressure-oxidation plant replaced a roaster facility in 1991. Several reasons were cited for the change (Frostiak and Haugard, 1992):

- improved gold recovery;
- improved environmental management, including no sulfur dioxide emissions and lower arsenic levels in tailings;
- lower cyanide consumption for oxidized slurry;
- higher grade of bullion recovered;
- lower gold inventory in the cyanide-leach operation and
- improved working environment.

Although air pollution has been reduced in several of the hydrometallurgical processes using autoclaves, there is an obvious shift for examining the extent of water pollution, whether increased or decreased, and the long-term stability of compounds formed during and after the autoclaving processes. Although significant debate continues on the merits of hydrometallurgical vs. pyrometallurgical processes, there appears to be consensus that the hydrometallurgical processes have a less adverse effect on the environment.

The Campbell Mine pressure-oxidation facility is discussed in more detail in Section 6.

In this modern world of environmental responsibility, pressure hydrometallurgy has made a positive contribution.

1.5. Pressure hydrometallurgy history

The first attempt to study a chemical reaction under pressure was in 1859 by the Russian chemist, N. Beketoff, while studying at the Sorbonne in Paris under Dumas (Habashi, 1971). Beketoff found that metallic silver can be precipitated from a nitrate solution that is heated under hydrogen pressure. In his experiments, for an autoclave Beketoff used a sealed glass tube containing the solution. Hydrogen was introduced from a side compartment of

Table 2
Some notable commercial pressure hydrometallurgical facilities

Metal	Feed type	Date (approximately)	Location	Temperature (°C)	Pressure (kPa)
Al	Bauxite ore	1900s	Worldwide	120–250	2,540–3,450
U	Pitchblende ore	1952	Saskatchewan, Canada	104	550
Ni	Sulfide con	1954	Alberta, Canada	80	410
Co	Arsenical con	1950s	Utah, USA	200	3,790
Zn	Sulfide con	1981	BC, Canada	150	1,030
Au	Whole ore	1985	California, USA	175	2,200
Au	Con	1986	São Bento, Brazil	190	1,600
Au	Whole ore	1990	Nevada, USA	220	2,890

the tube by the action of acid on zinc. Since that time there have been numerous investigations into processes that utilize leaching under oxidizing, neutral, or reducing conditions at elevated temperature and pressure to recover metals from ores and secondary materials. Several of these processes have been developed into full-scale plants, a list of which is given in Table 2.

Commercially, the first and probably best-known application of pressure hydrometallurgy was in the aluminium industry. In 1892, Bayer, an Austrian chemist living in Russia, patented a process for dissolving aluminium from bauxite by sodium hydroxide solution at a temperature above its boiling point (Habashi, 1971). The high temperature was needed so that dissolution could be achieved at a faster rate. This process is still being used in its original form without much major change. In the early Bayer plants dissolution was carried out batchwise but modern plants are continuous reactors, leaching times varying from minutes to a few hours, the leaching time being dependent on ore quality.

At the beginning of the 20th century, a great deal of work was done in pressure hydrometallurgy covering copper, nickel and cobalt metal recovery. Also, several chemists started using pressure vessels for a variety of reactions (Comings, 1956). As a result of developments, the chemical industry extensively uses pressure reactions, for example, in

- the synthesis of methanol;
- the synthesis of ethanol;
- the Haber process for ammonia synthesis (6,900 kPa);

- the synthesis of polyethylene (138,000 kPa) and
- the Fischer–Tropsch reactions for organic synthesis.

Pressure leaching of metal ores and concentrates using continuously operated autoclaves was first successfully applied commercially in the early 1950s. In parallel with developments in pressure leaching, significant work was conducted using such reducing gases as sulfur dioxide, carbon monoxide and hydrogen under pressure to effect final precipitation of metals directly from solutions, and several patents were granted (Schaufelberger, 1956; approximately 30 U.S. patents were granted to Schaufelberger and co-workers in the 1950s, details of which can be obtained from the U.S. Patent Office).

The necessary impetus to convert these interesting chemical reactions into commercial processes was provided during the period 1946–1955 by the group of research chemists and engineers assembled by E.S. Roberts at Chemical Construction Corporation (then a subsidiary of the American Cyanamid Company) to investigate hydrometallurgical processes for treating non-ferrous metal ores and concentrates. The motivation for the work was the need for improved extraction technology for leaner and complex ores, and the profit to be made from both construction of plants and licensing fees (Schaufelberger, 1956). The oxidizing pressure leaching of base metal sulfides probably did not become a viable treatment method until nearly 60 years after the Bayer process, due to the aggressive treatment conditions. Also, during the early part of the 20th century pyrometallurgical processes were in vogue and no impetus was apparent to replace these profitable processes for company shareholders. With the increased demand for base metals, and the improvement in materials of construction, the use of autoclaves using acid conditions, high-purity oxygen and elevated temperatures and pressures became possible.

In 1955, Chemical Construction Corporation was sold to Ebasco and the rights to the metals techniques sold to Sherritt–Gordon Mines Limited, a Canadian copper and nickel mining company, their first client. This plant used the ammonia pressure leaching process developed by F. Forward of the University of British Columbia, Canada, to leach nickel sulfide concentrate at 85°C and an air pressure of 420 kPa as the first step in a totally hydrometallurgical process to produce nickel powder and ammonium sulfate fertilizer. The plant is still in operation today at Fort Saskatchewan, Alberta, Canada. Also, two pressure-leaching plants were built to treat cobalt concentrates when cobalt prices were high after the Korean War but closed as the cobalt price declined (Berezowsky *et al.*, 1991).

During the 1970s, an acid pressure-leaching process was developed to treat zinc sulfide concentrates and first applied commercially in the Cominco zinc plant at Trail, British Columbia, Canada, in 1981. During the 1980s several new acid pressure-leaching plants were built to treat nickel–copper mattes for

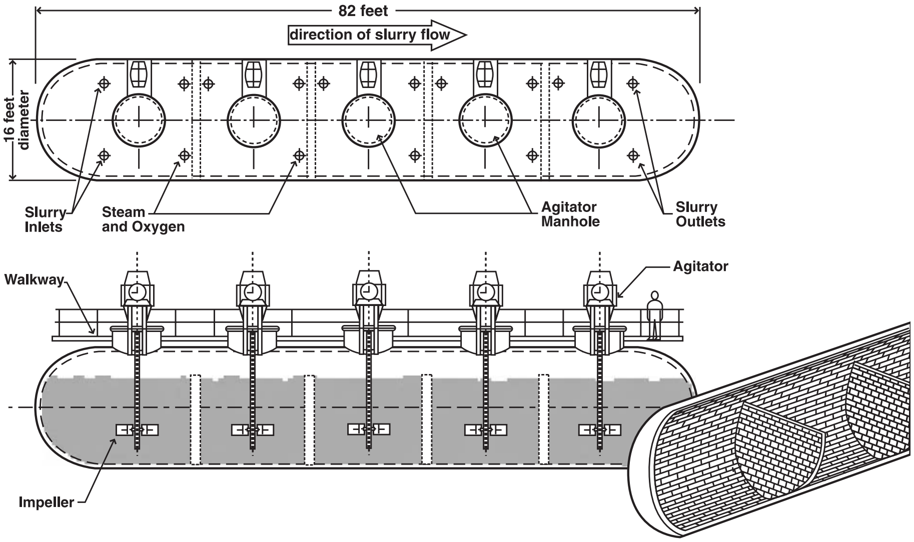

Fig. 2. Horizontal pressure oxidation vessel (Barrick Goldstrike Mine, USA).

the platinum mining industry. In 1959, the General Nickel Company commissioned a pressure acid-leach process for treatment of laterite nickel at Moa Bay, Cuba. This plant is still operating and two pressure acid-leach plants treating laterite nickel (Cawse and Murrin Murrin) are now operating in Western Australia.

The autoclave vessels used in the pressure hydrometallurgy processes for nickel, copper, zinc and cobalt have generally been horizontal vessels as depicted in Fig. 2. This shape was also adopted for processing gold ores and concentrates in the 1980s. However, pressure vessels can be kettles, spheres, pressurized pachuca tanks, towers, vertical autoclaves and pipe reactors. In the uranium industry, both vertical and horizontal autoclaves have been used commercially. The Bayer process generally uses agitated autoclaves with vertical steam piping.

2. GOLD PRESSURE OXIDATION

Within the gold industry two important steps have taken place in the pressure hydrometallurgy of ores. These are:

- pressure oxidation of whole ores using both alkaline and acidic processes, and
- pressure oxidation of concentrates.

Table 3
Process equipment for gold whole-ore vs. concentrate treatment

Equipment	Whole ore	Concentrate
Flotation plant	No	Yes
Splash/flash towers[a]	Yes	No
On-line boilers[b]	Yes	No
Slurry recirculation	No	Yes

[a] Recovery of process heat.
[b] Pre-heat only in concentrate treatment.

Although the autoclave is the central piece of equipment to both processes, the ancillary equipment associated with the autoclave is quite different. This is highlighted in Table 3.

Whole-ore treatment is utilized in processes where flotation gives poor gold and/or sulfide recovery to the concentrate. There is significant debate as to whether whole-ore or concentrate treatment is the better process when flotation is possible; suffice to say the optimum process is site- and ore-specific.

Sections 3–6 discuss the major features of these processes, with Section 5 providing a comparison of the acidic vs. alkaline options for whole-ore processing:

- whole ore – acidic;
- whole ore – alkaline and
- concentrate – acidic.

This review of the three processes will give an understanding of the unique features of the autoclave techniques.

3. ACIDIC PRESSURE OXIDATION – WHOLE ORE

The first gold pressure-oxidation plant commissioned was at the Homestake McLaughlin operation, CA, USA, in 1985 and served as the pioneering installation for whole-ore (acidic) treatment. The largest, by tonnes, of ore treated is Barrick Goldstrike, which is described below (Thomas and Williams, 2000).

3.1. Geology and mining

The Goldstrike property is located in Elko and Eureka counties in north-central Nevada, USA, on the Carlin geological trend. The mine is about 40 km northwest of the town of Carlin. The site is about 1,700 ft above sea level in the Tuscarora Mountains. Shallow, low-grade mineralization was discovered by diamond drilling in the Goldstrike area in the 1960s, and a heap-leach operation was established in the mid-1970s for this oxidized ore.

All of the gold in the sulfides is refractory, with 50% of the gold in refractory carbonaceous/sulfide ore. This makes autoclaving particularly important to Barrick. To treat this material an oxygenated roaster, at 11,000 t/d capacity, was commissioned in the second quarter of 2000.

The Goldstrike oxide mill, incorporating a carbon-in-leach (CIL) circuit, was expanded gradually over the years to its present day capacity of 16,000 t/d for the autoclave circuit.

3.2. Autoclave circuit

Fig. 3 shows a detailed representation of the autoclave circuit at Goldstrike.

Slurry from the grinding circuit, at approximately 35% solids and 80–85% passing 135 µm is pumped to three thickeners. Thickener underflow, at approximately 54% solids, is pumped to a train of four acidulation tanks. Sulfuric acid is added to the slurry to destroy sufficient carbonate (CO_3^{2-}) prior to entering the autoclave circuit. Process air is also injected into the acidulation tanks to aid in carbon dioxide removal. Carbonate levels are typically reduced to $<2\%$ in the acidulation tanks. As a rule of thumb, about 1% sulfide sulfur (S^{2-}) in the autoclave feed destroys 0.9% CO_3^{2-} and typ-

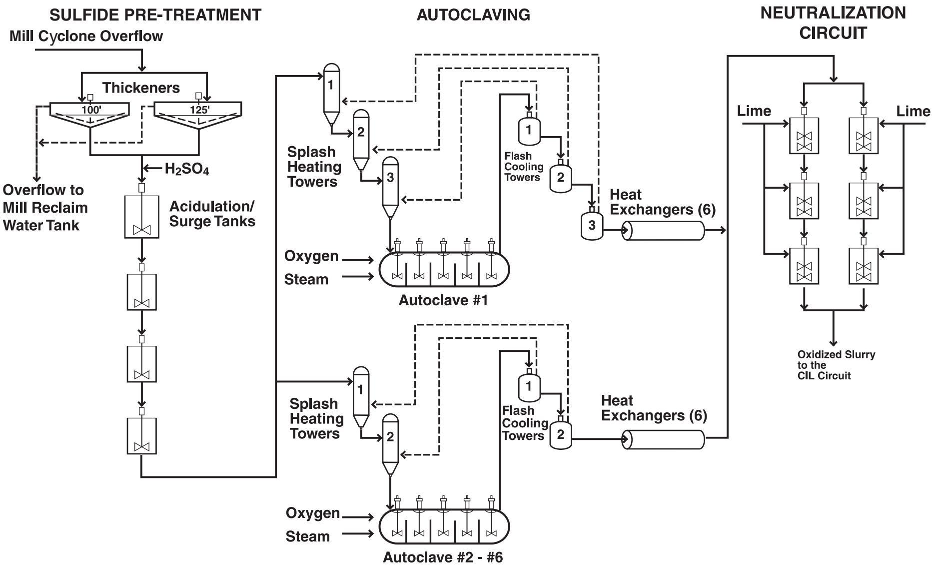

Fig. 3. Barrick Goldstrike autoclaving/pretreatment circuit (simplified flowsheet).

ically the autoclave feed ranges from 2.0 to 2.5% S^{2-}. At higher levels of S^{2-}, slightly $<0.9\%$, CO_3 is destroyed for each 1% S^{2-}.

The slurry is advanced from the acidulation tanks through a series of splash vessels before feeding into the autoclave. The slurry is preheated to a temperature of 165–175°C as it passes through the splash vessels. The heat source in the splash vessels is the flashed steam, which is released from the slurry discharging from the autoclave as it passes through the flash vessels. The slurry enters the splash vessels at the top and cascades down the internal baffles, while the flashed steam enters the lower section of the vessel and rises, contacting the slurry for direct heat transfer. The bottom of each vessel serves as a pump box for the inter-stage feed pumps.

The discharge from the high-pressure splash vessel is pumped by two positive displacement pumps into the autoclave. The pumps are operated in parallel with individual suction and discharge lines. Each pump can deliver approximately 60% of the required feed rate to the autoclave.

All six autoclaves have an outside diameter of 4.6 m: autoclave No. 1 is 23 m in total length, and autoclaves No. 2–6 are 25 m in total length. Each autoclave is divided into five compartments, with each compartment containing an agitator and injection pipes for oxygen, steam and water. Autoclave retention time ranges from 40–60 min and the vessel operates at approximately 2,900 kPa and 215–220°C. The lining of the autoclave vessels is 8 mm lead on the carbon steel shell, 3 mm with fibrefrax paper and 23-cm-thick acid brick.

Sulfide sulfur oxidation through the autoclave is typically of the order of 90–92%. Residual S^{2-} exiting the autoclave is targeted at less than 0.2%. Values greater than 0.25% S^{2-} typically result in poorer gold recoveries in the CIL circuit. Free-acid levels in the autoclave discharge are a function of S^{2-} and CO_3^{2-} in the autoclave feed, but normally range from 10 to 25 g/L.

The slurry exits the autoclave and passes through a series of flash vessels. Pressure and temperature are gradually let down to atmospheric pressure and 96°C, after passing through the flash cool-down circuit. The steam released by the instantaneous reduction in pressure through the flash vessel is ducted to the corresponding splash vessel. Slurry leaving the flash circuit is then cooled from 96°C to 48°C by shell and tube heat exchangers. The cooling water is on the shell side of the heat exchanger and the slurry passes through the tubes. In summary, the flash/splash system is a heat-recovery system, which minimizes the use of direct steam with inherent operating cost benefits. After the slurry passes through the slurry coolers it is pumped to two parallel trains of neutralization tanks, where the pH value is elevated from 1–2 to ~10.5.

Neutralized slurry from the pressure-oxidation circuit is pumped to two parallel streams of eight CIL tanks for gold extraction and subsequent recovery of gold in a conventional Zadra elution circuit.

Suitable ancillary facilities are installed to supply flocculant, sulfuric acid, oxygen, lime, steam and compressed air to the autoclave facility. The control system is a Bailey Network 90 distributed control system (DCS).

4. ALKALINE PRESSURE OXIDATION – WHOLE ORE

4.1. Geology and mining

The Mercur Mining District is located in the southern end of the Oquirrh Mountains, approximately 35 air miles southwest of Salt Lake City, USA. The district, primarily a gold producer, was organized in 1870 with the discovery of silver on Marion Hill in a massive jasperoid, termed the Silver Chert bed. Gold production did not commence until more than 20 years after the discovery of silver, as technology was not available for the economic recovery of gold as applied to the mineralogy at Mercur, where gold cannot be identified visually because of its micron size. Mercur became the first successful application in the USA of the McArthur-Forrest cyanide leaching process and was the earliest Carlin-type ore body mined in the USA (Wicks, 1987).

Gold was primarily deposited in favourable Paleozoic strata during the formation of sulfide–carbonate veins and occurs in oxidized ores as free, micron-sized particles. In unoxidized (refractory) ores, the micron-sized gold is associated with sulfide minerals and organic carbon such as kerogen and asphaltine. Oxidation of the Mercur deposit developed upwards progressively from the bottom of the deposit such that the upper portion of the deposit contains refractory ore. In October 1986, Barrick made the decision to engineer and install a 680 t/d addition to the Mercur mill to treat refractory ore. The mill was rated at 4,500 t/d, with 680 t/d of refractory material being batched through the grinding circuit.

Ore was selectively mined from open pits using the grade and CIL recovery cutoffs shown in Table 4.

This selective procedure allowed ore to be routed to the respective metallurgical facilities. The ore selection process was successful and relied heavily on foremen and shovel operators to selectively mine what was a mosaic of differing ore types.

Table 4
Barrick Mercur ore selection procedure

Ore type	Gold grade (g/t)	Projected CIL Recovery (%)
High-grade oxide	> 1.6	> 60
Low-grade oxide	1.1–1.6	> 60
High-grade refractory	> 2.0	< 60
Low-grade refractory	1.1–2.0	< 60
Heap leach	0.7–1.1	> 60 (cyanidation)

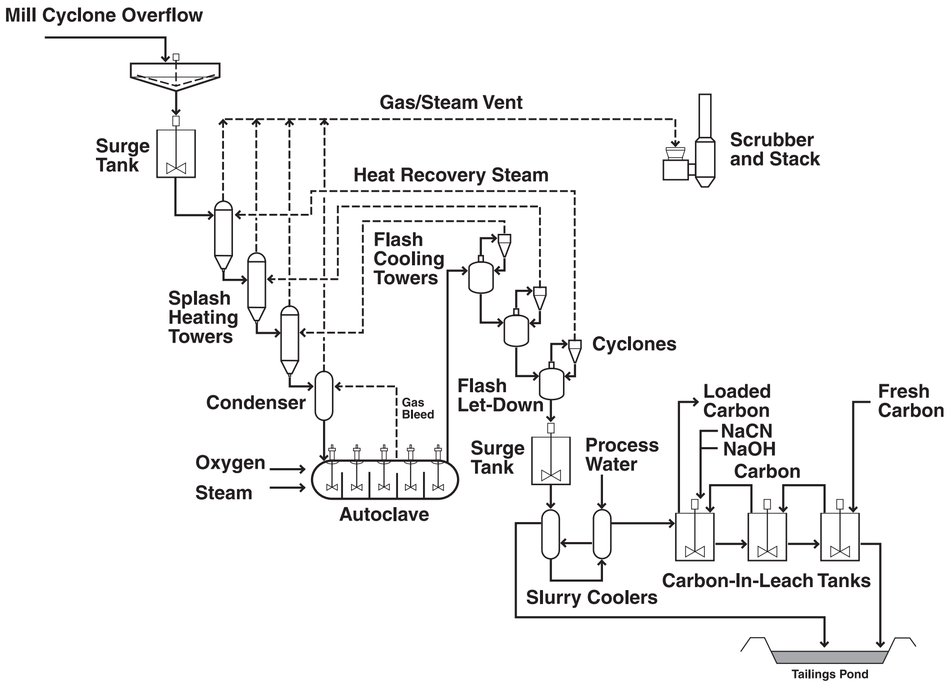

Fig. 4. Barrick Mercur refractory circuit (simplified flowsheet for pressure oxidation).

Autoclave Circuit

Fig. 4 shows a detailed representation of the autoclave circuit at Barrick Mercur.

The autoclave system utilized the existing crushing and grinding circuit and stored slurry in tanks for continuous autoclave processing. Ground slurry was thickened in a 20 m diameter, high-rate thickener to 50% solids and pumped to three stages of heat-up utilizing splash towers to which recycled steam from the autoclave discharge was introduced. Pumping was accomplished by one positive displacement pump (Geho). Pressure and temperature were raised from atmospheric and ambient to 3,135 kPa and 215°C, respectively. Slurry was then introduced into the autoclave, a horizontal, cylindrical unit, 3.7 m in diameter and 14 m long via a condenser. The autoclave was carbon steel and lined with a layer of acid brick refractory material. It was separated into four compartments by stainless-steel baffles. Each compartment was separately agitated by single-impeller mixers. The tip speed of the agitator blades was kept below 3.8 m/s to prevent accelerated wear on the blades. Also, the agitator impeller was set at one diameter above the brickwork to prevent brick erosion but still maintain solid suspension. Oxygen, supplied from a storage tank, was introduced to each autoclave compartment. Liquid oxygen was delivered by truck to a storage tank from a nearby oxygen plant. The oxygen was vaporized and introduced to each compartment. Exiting slurry passed through three stages of pressure letdown and flash steam was condensed in corresponding preheated splash tanks. Chokes were situated between each stage of letdown. Slurry residence time was typically 90 min.

Slurry from the final pressure letdown stage, at about 95°C, was pumped through heat exchangers to bring the temperature down to about 25°C for introduction to the CIL circuit. Three separate CIL tanks were dedicated to the autoclaved product to prevent any *preg-robbing* within the oxide circuit. After leaching, the slurry was introduced to the existing CIL tailings circuit. Loaded carbon from the CIL circuit was screened separately and introduced to the stripping circuit.

Sulfur content of the refractory ore averaged about 0.8% sulfide sulfur and required continual introduction of steam to the process. A 11,000 kg/h propane-fired boiler provided the required steam.

The Mercur autoclave circuit was shut down in February 1996 due to exhaustion of ore.

5. ACID AND ALKALINE AUTOCLAVE – COMPARISON

5.1. Chemistry

Generally, the gold recovery is lower and the residence time is longer in alkaline autoclaves. This can be explained by the chemistry of the two processes.

The objective of the pressure oxidation/autoclaving process is the destruction of the sulfides, such as pyrite, marcasite or arsenopyrite, thereby liberating the occluded gold. The gold is then amenable to recovery by the cyanidation process.

5.1.1. Acid chemistry

For an acid autoclave operating at temperatures greater than 175°C and a pH value below 2, the reactions can be represented (Thomas, 1994) as

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2FeSO_4 + 2H_2SO_4 \quad (6)$$

$$2FeSO_4 + H_2SO_4 + \tfrac{1}{2}O_2 \rightarrow Fe_2(SO_4)_3 + H_2O \quad (7)$$

$$Fe_2(SO_4)_3 + 3H_2O \rightarrow Fe_2O_3(\downarrow) + 3H_2SO_4 \quad (8)$$

The highly oxidizing state in the acid autoclave is important as ferrous sulfate is converted into ferric sulfate (Eq. (7)). This reaction is beneficial because ferrous sulfate consumes cyanide in the cyanidation step, and this increases operating costs.

In acid autoclaving, silver is precipitated as argentojarosite [$Ag_2Fe_3(SO_4)_4(OH)_{12}$] but can be recovered by a lime-boil pretreatment process.

Kinetic factors are particularly important in acid pressure oxidation. Below 175°C, elemental sulfur (S°) forms. Its production is to be avoided as it can reduce gold recovery by encapsulating gold in the subsequent cyanidation step and also coating unoxidized sulfide particles during autoclaving preventing complete oxidation. Elemental sulfur can also form thiocyanate during cyanidation, thereby increasing operating costs. Above 175°C, oxidation rates and pressures increase with increasing temperature. Autoclaves are designed to operate within 175–230°C to minimize capital costs. At these temperatures, reasonable steel-shell thickness is achieved to manufacture the autoclave and adequately contain the pressure.

5.1.2. *Alkaline chemistry*

The Mercur refractory ore contained up to 20% carbonates and accordingly, sulfuric acid produced by the oxidation of the pyrites was immediately neutralized to create an alkaline environment. Reaction (9) is considered a typical representation of the chemistry (Fleming *et al.*, 1998):

$$2FeS_2 + 7.5O_2 + 4CaCO_3 \rightarrow Fe_2O_3(\downarrow) + 4CaSO_4 + 4CO_2(\uparrow) \quad (9)$$

Gold recovery by alkaline autoclaving is generally up to 10% lower than in acid autoclaving and is related to gold entrapment in the oxidation products and encapsulation of unoxidized sulfides. In acid autoclaving the product of oxidation, ferrous sulfate, is soluble in acid solution and will diffuse away from the reacting pyrite surface, hydrolysing and precipitating as hematite [Fe_2O_3]. In alkaline autoclaving the hematite forms at the oxidizing surface, entrapping gold and thereby reducing gold recovery.

Wherever possible, alkaline autoclaving should be considered, because materials of construction are more conventional and therefore, reduce capital and operating costs.

The alkaline circuit was attractive to Mercur as it offered low capital and operating costs, satisfactory recovery and no associated mining costs. The mining costs were borne by the oxide ore body as in this unusual case the

Table 5
Materials of construction for autoclave facilities (wetted surfaces)

Item	Barrick Goldstrike	Barrick Mercur
Mediu	Acid	Alkaline
Autoclave discharge pH	1.2–2.0	7.5–8.5
Splash/flash/autoclave	Acid-proof brick	Acid-proof brick
Mortar in autoclave	WiPiSe/Hydromet 50	SEMAG
Inter-stage pumps (splash)	High-Cr iron	High-Cr iron
Geho		Nodular cast-iron
Housing	CD4MCu	Stellite-coated steel
Valves	CD4MCu	EPDM
Diaphragm	EPDM	
Injection tubes	Ferralium 255	Inconel 625
Autoclave agitator	Titanium	316 L stainless steel
Flash valve body	Titanium	Hastaloy C
Flash choke	Ceramic Hexoloy SA	Ceramic Hexoloy SA
High-pressure steam duct	Titanium	316 L stainless steel
Low-pressure steam duct	316 L stainless steel	316 L stainless steel
Cooler feed-pumps	EPDM	High-Cr iron
Cooler shell	Carbon steel	Carbon steel
Cooler tubes	316 L stainless steel	316 L stainless steel

refractory ore was overburden. Classification of the refractory ore as overburden made the autoclave project financially viable.

5.2. Materials of construction

The selection of the process chemistry, alkaline or acid, has a significant impact on the capital costs. Table 5 highlights the less expensive materials used for constructing alkaline facilities (Thomas, 1991). Acid autoclaving uses exotic materials of construction, which increase capital and operating costs. For example, the autoclave discharge valve, made of titanium, costs approximately US$120,000 to replace at present.

5.3. Operating cost

The Mercur alkaline and Goldstrike acid autoclave operations display a marked difference in operating costs (Thomas, 1994), as detailed in Table 6.

Reagent costs at the acid circuit were higher and reflect the acid required to remove carbonates prior to autoclaving and lime required for subsequent neutralization. The combined cost of acid and lime for the acid circuit is approximately US$3.25/t. Propane costs for the acid circuit are lower, reflecting the higher sulfide sulfur content of the ore, 2.5% vs. 1.0% for the alkaline circuit.

Table 6
Operating cost difference for Barrick alkaline/acid autoclaves (US$/$t^a$)

Cost item	Barrick Goldstrike	Barrick Mercur
Labour	1.63	1.72
Reagents and oxygen	1.26	5.44
Maintenance	2.85	3.13
Propane (heat)	2.28	0.69
Electricity	0.35	1.76
Total	8.37	12.74

[a] Crushing, grinding, CIL and refinery excluded.

Although maintenance costs at the Goldstrike (acid) circuit are only slightly higher than the Mercur (alkaline) circuit, despite the more exotic materials of construction, the acid circuit's relatively low figure represents significant maintenance improvements over a decade. In the early years, maintenance costs for Goldstrike (acid) were between US$4.50 and US$5.00/t.

The alkaline autoclave environment is far less aggressive than the acid counterpart; accordingly, capital and operating costs are significantly less.

Gold recoveries by alkaline autoclaving are typically lower than by acid autoclaving and are related to the reactions products not being dispersed from the oxidizing surface, thereby trapping and encapsulating gold. Accordingly, depending on the specific ore deposit, acid autoclaving is the preferred circuit.

Alkaline autoclaving is attractive with high carbonate-content ores, such as those at Mercur.

6. ACIDIC PRESSURE OXIDATION – CONCENTRATE

Fig. 5 depicts a circuit for gold recovery from a concentrate using autoclaves. The sulfides are floated into a concentrate ahead of the autoclave circuit followed by acid pretreatment. Prior to autoclaving the slurry is thickened in a thickener, acidic overflow passing to a waste-treatment plant. The sulfide concentrate has sufficient sulfides to allow an autogenous reaction in the autoclave, thereby precluding the need for splash/flash towers as in whole-ore treatment. The towers are the heat-recovery system for the whole-ore treatment route, thereby reducing indirect heating costs.

Autoclave discharge passes to a counter-current decantation (CCD) wash circuit, which has two functions:

- Recycling of the thickener overflow to acidify the feed prior to autoclaving (with the claim of minimizing fresh-acid costs).

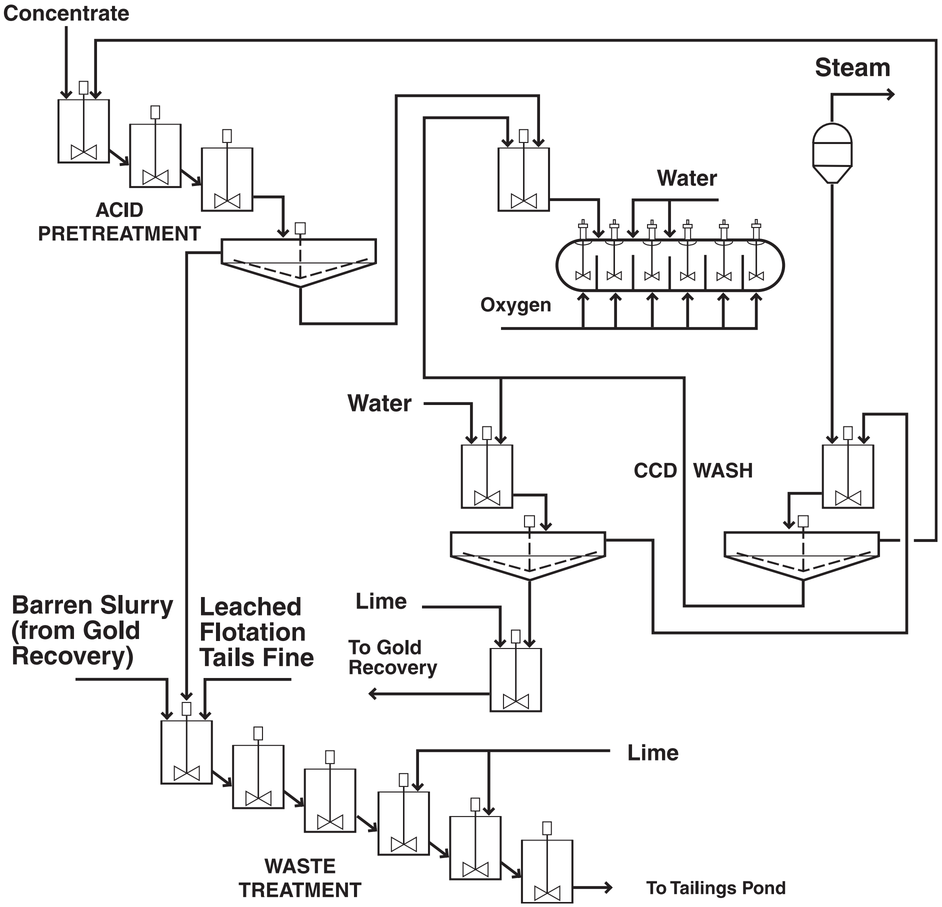

Fig. 5. Campbell Mine pressure-oxidation plant.

- Partial recycle of the thickener underflow to prevent agglomeration (with the claim of recycling product and providing a greater surface area for sulfur deposition. More reactive sulfides have a propensity to form elemental sulfur as an intermediate oxidation product (Berezowsky *et al.*, 1991).

After the CCD wash circuit, the slurry is neutralized and forwarded to gold recovery by cyanidation.

The Placer Dome Campbell Mine facility was commissioned in July 1991 and represents one of the early autoclaves to treat an auriferous (Au: 213 g/t) sulfide concentrate with relatively high arsenic (10%) and sulfur (18%) contents. The first was São Bento in Brazil. Economic and environmental advantages claimed (Frostiak and Haugard, 1992) for the Campbell circuit over roasting have been highlighted earlier in this chapter (Section 1).

The Campbell autoclave has the following operating statistics:

- Temperature: 190–195°C
- Pressure: 2,200 kPa
- Size: 2.75 m diameter
- Throughput: 55 t/d per autoclave
- Number of Autoclaves: 1

In the autoclave the arsenopyrite is oxidized producing sulfuric acid and a ferric arsenate compound. Chemical reactions may be written as follows:

$$4FeAsS + 11O_2 + 2H_2O \rightarrow 4HAsO_2 + 4FeSO_4 \quad (10)$$

$$4FeSO_4 + 2H_2SO_4 + O_2 \rightarrow 2Fe_2(SO_4)_3 + 2H_2O \quad (11)$$

$$2HAsO_2 + O_2 + 2H_2O \rightarrow 2H_3AsO_4 \quad (12)$$

$$Fe_2(SO_4)_3 + 2H_3AsO_4 \rightarrow 2FeAsO_4 + 3H_2SO_4 \quad (13)$$

The ferric arsenate produced above 150°C is considered to be crystalline. At room temperature the ferric arsenate produced from simulating high-temperature autoclave conditions is considered to be stable up to a pH value of approximately 8. Any residual arsenic remaining in the solution leaving the autoclave is neutralized by lime, forming a complex calcium–ferric–arsenate–sulfate phase. Significant work has been conducted at Imperial College, University of London (*e.g.*, Neira Arenas and Monhemius, 1998), to obtain a greater understanding of arsenic-compound stability related to autoclave technology.

Table 7
Operating costs for a 1,360 t/d gold pressure-oxidation plant

Plant type	Operating cost (C$/t)
Oxide mill	8
Roasting	17 (*i.e.*, 8 + 9)
Acidic autoclave	21 (*i.e.*, 8 + 13)

Table 8
Gold recoveries by process

Procedure	Gold recovery (%)
CIL	15
Roasting	80
Acidic autoclave	90

Table 9
Capital costs for a 1,360 t/d gold pressure-oxidation plant

Circuit	Capital cost (US$ millions)
Mill[a]	20
Mill + alkaline autoclave	36 (*i.e.*, 20 + 16)
Mill + acidic autoclave	50 (*i.e.*, 20 + 30)

[a] Includes crushing, grinding, CIL and gold recovery.

Table 10
Summary of gold pressure-oxidation plants

Plant	Company	Location	Feed	Capacity (t/d)	Temperature (°C)	Start-up
McLaughlin	Homestake	USA	Ore	2,730	180	1985
São Bento	Gencor	Brazil	Concentrate	240	190	1986
Mercur	Barrick	USA	Concentrate	680	225	1988
Getchell	First Mississippi	USA	Ore	2,700	210	1989
Goldstrike	Barrick	USA	Ore	1,825	225	1990
Porgera	Placer Dome	PNG	Concentrate	1,215	195	1991
Campbell	Placer Dome	Canada	Concentrate	71	195	1991
Goldstrike	Barrick	USA	Ore	4,700	225	1992
Con	Royal Oak	Canada	Concentrate	90	210	1992
Goldstrike	Barrick	USA	Ore	7,065	225	1993
Lone Tree	Newmont	USA	Ore	2,270	190	1994
Twin Creeks	Newmont	USA	Ore	7,260	225	1996
Lihir	Rio Tinto/ Nuigini	PNG	Ore/concentrate	8,100	210	1997
Hillgrove	Hillgrove	Australia	Concentrate	24	220	1999
Macraes	OceanaGold	New Zealand	Concentrate	20	225	1999

7. PRESSURE-OXIDATION SUMMARY

The utilization of a pressure-oxidation circuit to treat refractory gold ores or concentrates is a complex decision, taking into consideration capital costs, operating costs, gold recovery and environmental impacts. Tables 7–9 highlight the interacting variables, based on Goldstrike refractory ore at 1,360 t/d throughput.

The payback and internal rate of return (IRR) has to be evaluated in the decision for selecting the process. Each project is site-specific, being influenced by air- and water-quality discharge requirements and ore type. The example serves to indicate the complexity in choosing the correct process. Also, the off-gases from autoclaves are significantly cleaner than the off-gases from roasters, when direct off-gases are compared without cleaning. Consequently, the autoclave gas-cleaning equipment is simpler and comprises less units. The gas from the scrubber stack is over 90% steam with minor quantities of oxygen, carbon dioxide and inerts.

The first pressure-hydrometallurgy gold facility was McLaughlin in 1985, treating a whole ore. This was closely followed by a concentrate facility at São Bento in Brazil in 1986 and the Mercur alkaline whole ore facility in 1988. Between 1988 and 1993 Goldstrike constructed six autoclaves for an ultimate capacity of 16,000 t/d.

Over the past 20 years several pressure-oxidation facilities have been built for gold ore and concentrate treatment (Table 10). Pressure hydrometallurgy offers an economical and an environmentally compatible process for treating certain refractory gold ores.

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Chapter 16

Bacterial oxidation of refractory gold concentrates

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This chapter reviews commercial bacterial-oxidation practice and considers some of the design and operational characteristics of bacterial-oxidation plants for the treatment of refractory gold concentrates. New process advancements are discussed, which improve the cost effectiveness of bacterial oxidation for the treatment of concentrates by improving the rate of oxidation and reducing cyanide consumption in downstream gold recovery. These advancements have arisen as a result of laboratory investigations combined with observations made on existing plants. Refinements to the bacterial-oxidation process, which alter the sulfur chemistry of the final residue, have been found beneficial in reducing cyanide consumption. The process features identified, which create an oxidized residue more amenable to cyanidation, are:

(i) The preferential removal of process liquor during bacterial oxidation (*liquor stripping*), which reduces the concentration of soluble elements present in the final pulp.
(ii) A finer particle size of feed to the bacterial-oxidation process.
(iii) Small extensions to the residence time of the bacterial-oxidation process.

Preferential removal of liquor, either on its own or in combination with a finer feed sizing, can improve the rate of oxidation. For some refractory concentrates, ultra-fine grinding of concentrate feed may marginally improve gold recovery by increasing the exposure of siliceous gold. The chapter

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includes a brief comparison of bacterial oxidation with the alternative treatment methods, which are normally considered when defining the most economic processing route for a refractory gold operation.

1. INTRODUCTION AND BACKGROUND

Bacterial oxidation is now considered to be a proven commercial technique for the treatment of refractory sulfide gold concentrates. Since 1986 the technique has been applied successfully on a commercial scale for the removal of arsenopyrite and pyrite to give high gold extractions on cyanidation (Van Aswegen *et al.*, 1989). A chronology of gold projects, recognized as using agitated aerated bioreactors for sulfide oxidation prior to cyanidation, is given in Table 1. It is evident that bacterial oxidation has been applied at a wide variety of locations and at different scales of throughput. Stirred-reactor technology has to date been reserved for the treatment of concentrates as opposed to whole-ore treatment, with the exception of a single project at Tonkin Springs in Nevada, USA (Foo *et al.*, 1990). Clearly, the wide differences in composition of the materials treated are testimony to the ability of bacterial oxidation to be considered for a broad spectrum of projects. The demonstration over time that bacterial oxidation can be both economically competitive as well as being a relatively simple, environmentally responsible and robust operation, has being instrumental in encouraging these new applications. Additional testimony for the continuing emergence and acceptance of bacterial oxidation is provided by evidence that the number of bacterial-oxidation plants for gold concentrate treatment now rivals that for pressure leaching. Excellent publications are already available describing either the fundamental aspects of bacterial oxidation (Torma, 1997) or its application to specific projects (Budden and Bunyard, 1994; Brown *et al.*, 1994; Bell and Quan, 1997; Miller *et al.*, 2004). It is not the aim to duplicate such publications, but to present a summary of the design and operational characteristics of bacterial oxidation that are emerging as a result of its wider commercial use.

In a quest for improvement, the effectiveness and economics of any unit operation such as bacterial oxidation cannot be assessed in isolation to the upstream and downstream operations with which it is integrated. For oxidation pre-treatment, it is necessary to consider the consequences of the oxidation process on the total flowsheet and in particular that of downstream gold recovery. Although there have been many excellent research and development programmes to improve features of the bacterial oxidation operation itself (Oolman, 1993; Pinches *et al.*, 1994), aspects which improve its integration into gold extraction and recovery also need to be addressed.

Table 1
Chronology of recognized commercial bacterial-oxidation plants for refractory gold processing

Plant and Location	Operating Years	Design Capacity (tpd concentrate)	Total Reactor Volume (m^3)	Approximately % S^{2-} in feed	Technology Supplier	Reasons for Closure (if Applicable)	Reference
Fairview, South Africa	1986–present	10 (1986) 35 (1991) 40 (1994) 55 (1999)	1,260	18–24	BIOX®	Not applicable	Van Aswegen (2004)
Tonkin Springs, Nevada, USA	1989–1990	1500 (whole ore)	8,800	1.3	Own installation	Funding constraints and technical issues	Foo *et al.* (1990)
São Bento, Brazil	1990–present	150 (1990) 300 (1994) 380 (1997)	1,300	19	BIOX®	Bacterial oxidation section shut down for energy saving	Suttill (1990); Van Aswegen (2004)
Harbour Lights, Western Australia	1992–1994	40	980	18	BIOX®	Ore depleted	Brierley (1995)
Wiluna, Western Australia	1993–present	115 (1993) 158 (1995)	4,230	24	BIOX®	Not applicable	Brown *et al.* (1994)
Sansu, Ashanti, Ghana	1994–present	720 (1994) 960 (1995)	21,600	11	BIOX®	Not applicable	Nicholson *et al.* (1994)
Youanmi, Western Australia	1994–1998	120	3,000	28 (partial oxidation)	BacTech	Ore depleted (high mining costs)	Miller (1997)

Table 1 (*continued*)

Plant and Location	Operating Years	Design Capacity (tpd concentrate)	Total Reactor Volume (m^3)	Approximately % S^{2-} in feed	Technology Supplier	Reasons for Closure (if Applicable)	Reference
Proano, Tamboraque, Peru	1999–2003	60	1,800	30	BIOX®	Low grade (high mining costs)	Loayza and Ly (1999)
Beaconsfield, Tasmania	2000–present	60–70	2,241	27–34	BacTech Mintek	Not applicable	Pinches *et al.* (2000)
Laizhou, Shandong Province, China	2001–present	100 = 120	4,050	21–25	BacTech Mintek	Not applicable	Miller *et al.* (2004)

In particular, the desire to reduce cyanide consumption for some bacterial-oxidation operations has been recognized, and this provided a focus for the authors to consider a number of process modifications to bacterial oxidation, which would improve the cyanidation characteristics of the oxidized residue. In the programme of work described in this chapter to investigate this phenomenon, it was not immediately intuitive that modifications to the bacterial-oxidation process, resulting in changes to the residue cyanidation characteristics, could also aid the rate of oxidation.

Making better use of the *oxidation capacity* of a plant while reducing cyanide consumption are clearly the key factors to increasing the cost effectiveness of bacterial oxidation. The following section gives a summary discussion of the results developed over a number of years and illustrates the common link of certain parameters influencing both the cyanidation characteristics of the residue and the rate of oxidation.

2. CURRENT BACTERIAL-OXIDATION PLANT DESIGN AND PRACTICE

In general terms many applications of bacterial oxidation for refractory gold concentrate treatment have a relatively common flowsheet, which incorporates crushing, milling, concentrate production by flotation, bacterial oxidation of concentrate, followed by cyanidation and gold recovery from the oxidized residue. However, the complexity of the overall processing plant and, hence, the integration of bacterial oxidation into the flowsheet is clearly project-specific. An excellent example of a more recent integration into a gold-processing flowsheet has been given by Pinches *et al.* (2000). Fig. 1 shows the complement of unit operations employed at Beaconsfield Tasmania, which incorporates both a gravity and flotation circuit prior to bacterial oxidation.

Irrespective of the upstream operations before bacterial oxidation, the process philosophy is relatively common to all flowsheets that incorporate this unit process. Concentrate feed for bacterial oxidation is generally diluted with addition of water to the working pulp density of between 15 and 20% (m/m). Commercial installations use a staged sequence of agitated aerated reactors for continuous treatment of pulp, with an overall residence time that allows for the growth and division of the bacterial population to ensure its retention within the system. The reaction is exothermic and reactors are cooled with water to maintain a set temperature generally between 42 and 50°C, dependent upon the bacterial culture in use (Brown *et al.*, 1994; Budden and Bunyard, 1994). Overall residence times have been as low as 3.5 days when a partial oxidation is conducted (Miller, 1997), but in the majority of cases a high level of oxidation is required and 5–6 days is a common residence time.

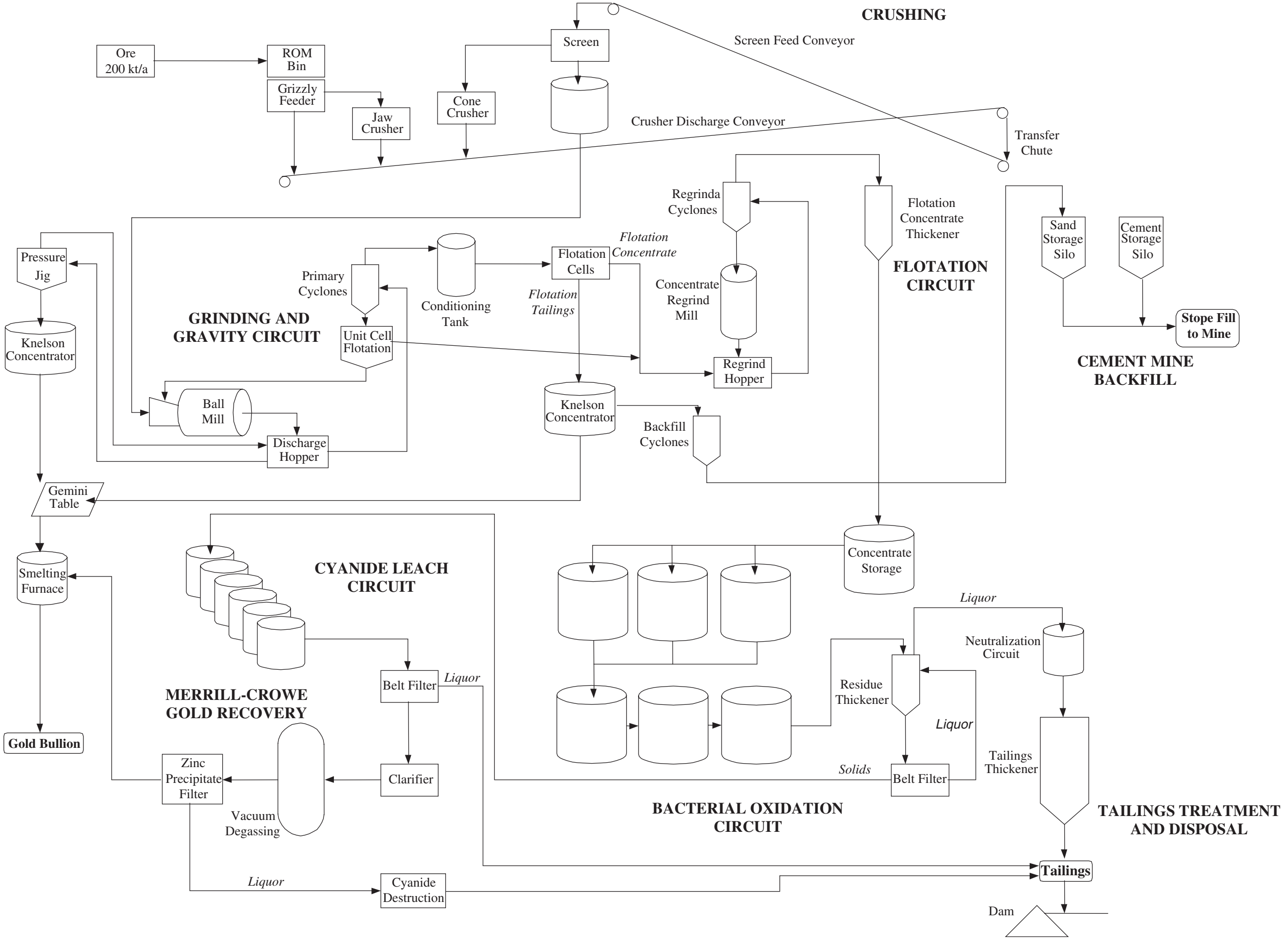

Fig. 1. Beaconsfield flowsheet illustrating the integration of bacterial oxidation into a gravity/flotation circuit (after Pinches *et al.*, 2000).

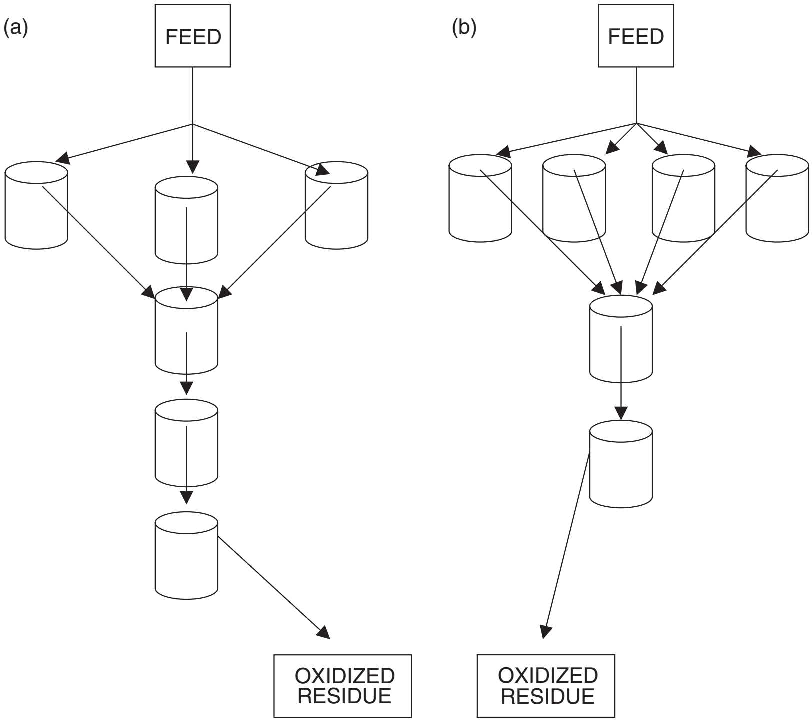

Fig. 2. Reactor circuit configurations used in bacterial-oxidation processing. (a) Conventional practice of three primary reactors in parallel and three secondary reactors in series; (b) alternative of four primary reactors in parallel and two secondary reactors in series.

Fig. 2 illustrates the conventions for circuit configurations of bacterial-oxidation reactors. It is normal practice for the feed to be divided equally between primary reactors, which operate in parallel, and for the partially oxidized product exiting from the primary reactors to be recombined and enter a series of secondary reactors. This usually gives the primary reactors at least double the residence time of the secondary reactors and ensures adequate time in the primary reactors for growth and division of the bacteria to prevent *washout*. It is typical practice for at least two-thirds of the total oxidation requirements to take place in the primary reactors. The majority of plant will operate in a *3.1.1.1* sequence, which is to say: three primary reactors operating in parallel followed by three secondary reactors operating in series.

This provides an overall four-staged system, which is conventional for minimizing short-circuiting and, in practice, typically achieves a 95% oxidation level. Many plants have the capability to also operate a *4.1.1* sequence using four primary reactors followed by two secondary reactors in series. Although this provides a method of increasing plant throughput, short-circuiting can be increased as a result of the three-stage system. However, it is sometimes used successfully as a means to increase the rate of gold production by increasing plant throughput. This configuration has also been used on some sites as a method of removing heat more effectively if very high summer temperatures impose constraints on the cooling system, which would otherwise lead to decrease in plant throughput. Oxidized pulp leaving the last secondary reactor is taken forward to solid/liquid separation and washing. Usually a three-stage counter-current decantation system is adequate to reduce soluble-iron levels to below 0.5 g/L before cyanidation. Filtration, however, has been used at two installations (Pinches *et al.*, 2000; Miller *et al.*, 2004) and is finding favour as an alternative to counter-current decantation due to the smaller footprint and lower volumes of wash water combined with more effective washing of the residue. Clearly, the production of filter cake as opposed to a thickened underflow at 40–50% solids also allows more water to be retained for recycle within the bacterial-oxidation and liquor-neutralization circuits.

Liquor neutralization is usually performed using local limestone in a staged series of agitated reactors, while the more powerful neutralization quality of lime is sometimes used as an alternative if this is more economic due to high transport costs. Neutralization produces a precipitate containing ferric arsenate, which is dispatched to tails as benign stable compounds. The long-term environmental stability of ferric arsenate compounds has been the subject of investigations (Nyombolo *et al.*, 2000) and it is generally concluded that if the neutralization is conducted in a controlled manner and the ferric-to-arsenic ratio in the liquor exceeds ~ 3, then the precipitates will have a good long-term stability for disposal (Krause and Ettel, 1989; Ringwood, 1995). Filtration of precipitate is also in use at the most recent bacterial-oxidation plant to be commissioned, at Laizhou in China, resulting in a considerable reduction in volume for tailings disposal as well as maximizing the availability of recycle water for direct reuse in the bacterial-oxidation process (Miller *et al.*, 2004).

For downstream processing, the pH value of the oxidized residue is adjusted with lime prior to gold leaching with cyanide. Often the addition of antifoam is required to reduce foam formation during cyanidation. Both the carbon-in-leach (CIL) and Merrill-Crowe processes have been used successfully for gold recovery from bacterial-oxidation residues.

2.1. Agitation, aeration and reactors

Treatment of sulfide concentrates by bacterial oxidation in reactors has created an almost unique duty for agitation and aeration (Kubera and Oldshue, 1992; Fraser, 1993). The hydrofoil designs for agitators developed in the mid-1980s have quite suitable characteristics for use in bacterial oxidation (Lally, 1987). The mixing and solids suspension is good, gas-transfer coefficients are comparable to turbines and power requirement is reduced. Despite these features, large airflows are a recognized characteristic of bacterial-oxidation reactors, owing to utilization factors generally between 30 and 40%, combined with the high demand for oxygen in the reaction. Air-to-sulfide ratios of between 25,000 and 30,000 Nm^3/tonne of sulfur are common values in design. The required power input for agitators is primarily a function of airflow and the combined power of agitation and air supply by blowers represents the most significant component of operating costs for most bacterial-oxidation plants. Together with the cost of reactor tankage, the capital costs for these areas are also significant. The large volume needed for oxidizing a dilute pulp over a residence time of a few days implies large tank sizes, while the acidic nature of the pulp and often the consideration of water quality, requires the use of rubber-lined steel or specialized steels as materials of construction, which includes SAF2205 (Miller, 1997) and other high-grade stainless steels (Ritchie and Barter, 1997).

Many research-and-development activities have investigated possible methods to reduce agitation and aeration power requirements with the objective of decreasing operating costs and, where possible, capital costs (Atkins and Pooley, 1983; Van Weert and Kroes, 1993; Boon and Heijin, 1998). The selected agitator must efficiently disperse all the air while ensuring that flooding is avoided; the size of the agitator is thus a function of the air-expansion thermodynamics. Trials of some innovative agitation/aeration systems have been made at demonstration scale and also on commercial plants; however, little information has been made available to suggest any advantage over the agitation/aeration combinations used in conventional plants. A specific agitator power of 30–35 Nm^3/h of air per installed kW is often used for conventional agitator sizing and it is generally considered that the conventional power requirement for agitation is between 0.2 and 0.3 kW/m^3 of reactor volume (these values are installed power and not drawn power).

Although these have become industry standards, which have yet to be seriously challenged, development of agitation systems will continue to be a considerable area of interest for research-and-development programmes. In the future, these studies may lead to reductions in power requirements with improved combinations of agitator/air-sparging systems in association with more cost-effective blower performance. The use of air enriched with oxygen has also been considered. However, desktop studies by the authors examining the use of pressure-swing absorption (PSA) devices have not suggested economic advantages for this concept, but such concepts need frequent re-evaluation, as technology improvements and cost reductions for creating oxygen enrichment may well be a future realization.

As already mentioned, the capital cost of tankage is also a significant cost component, and there have been examples of development activities aimed at reducing these costs (Greenhalgh and Ritchie, 1999), which have yet to be tested over time in commercial installations. These include examinations of lower-cost alternatives for materials of construction and the potential for new reactor concepts aiming to alleviate the limitations of reactor scale-up that are currently imposed (Harvey *et al.*, 1999).

2.2. Bacterial-oxidation reagent consumption

Nutrients are a minor component of reagent costs for bacterial-oxidation processing, whereas acid if required for pH control can be significant. Clearly, this is dependent upon the carbonate content of feed, site-specific reagent costs and the efforts made to achieve a good acid balance in flowsheet design. The cost of reagents for neutralization of final liquor may be significant if cheap local limestone cannot be supplied or the cost of transport is high, hence, favouring the use of lime. Many projects have a local source of limestone, however, and neutralization costs are in these cases not a defining feature for project viability. Many ores have a carbonate gangue component, which is largely rejected in flotation (see Chapter 14). The carbonate tailings from flotation can then be used in bacterial-oxidation liquor neutralization to partially offset the limestone requirements. However, the presence of some carbonates in bacterial-oxidation feed is considered desirable in order to supplement the carbon dioxide source that is required for bacterial growth (Pinches *et al.*, 1994; Jaworska and Urbanek, 1995). Carbon dioxide is otherwise obtained only from the quantities present in the air supplied to the reactors.

2.3. Cyanide consumption of bacterially-oxidized residue

When cyanide-leaching bacterial-oxidation products, the consumption of cyanide per tonne of residue has tended to be relatively high due to the presence of cyanicides in the residue (Hackl, 1989; Komnitsas and Pooley, 1990; see also Chapter 20). When treating concentrates with a high gold-to-sulfide ratio and with a high mass loss during oxidation, the consumption of cyanide when expressed as kilograms per tonne of whole ore is not an excessive cost. However, even when treating these residues there can still be a significant unnecessary wastage of cyanide. For ores and concentrates with a lower gold-to-sulfide ratio the cost of cyanide for a project can therefore be very significant.

The problem of the high cost and consumption of cyanide is compounded if the CIL tailings have to be detoxified prior to discharge. If the detoxification only requires removal of weak acid dissociable (WAD) cyanide species, the cost of the detoxification process will usually be approximately equivalent to the cost of cyanide. If it is a requirement to remove thiocyanates as well as WAD cyanide species, the cost of detoxification can be a factor of 3–5 times the cost of the cyanide and this can either make projects

Table 2
Cyanide consumptions noted for the treatment of bacterial-oxidation residues from testwork investigations and design criteria for commercial plants

Concentrate Origin	Feed Concentrate Analysis			% Sulfide Oxidation	% Gold Extraction	Cyanide Consumption (kg/t conc.)	Information Origin
	% S^{2-}	% Fe	% As				
Ashanti/Sansu	11	18	8	95	93–96	15	Design (Nicholson *et al.*, 1994)
Wiluna	24	24	10	90	94–98	30	Design (Brown *et al.*, 1994)
Youanmi	28	26	4	32	90–95	8	Design/actual (Miller, 1997)
Vaal Reefs	30	25	0	49	85	5	Piloting, continuous (Pinches *et al.*, 1994)
Olympias	37	39	13	34	55	37	Testwork (Komnitsas and Pooley, 1990)
				57	73	87	Testwork (Komnitsas and Pooley, 1990)
				72	79	122	Testwork (Komnitsas and Pooley, 1990)
Australia	32	32	6	92	96	5	Testwork, batch (Wilkinson, 2000)
Northern Europe	31	31	7	95	95	2–5	Testwork, batch (Wilkinson, 2000)
				95	95	14–25	Testwork, continuous (Wilkinson, 2000)
Laizhou China	20–25	20–25	4–7	95	97	2–3	Design/actual (Miller *et al.*, 2004)

uneconomic or significantly less attractive. Clearly, there are major incentives for many projects to reduce cyanide usage.

Table 2 summarizes information from the literature on the cyanide consumptions noted for the treatment of bacterial-oxidation residues from both testwork investigations and commercial plants. Hack1 and Jones (1997) presented an earlier version of similar information and noted that cyanide consumptions in the treatment of bacterial-oxidation residues vary widely and seem to be feed-specific. More recent information included in Table 2 supports this premise. In general terms, it would appear that lower cyanide consumptions are associated with plants that have a lower quantity of sulfide in the feed. The results presented in Table 2 also suggest that higher cyanide consumptions are evident from continuous processes compared to laboratory cyanidation tests using residues from batch bacterial-oxidation tests. The difference in cyanidation characteristics of the residues would appear to be influenced by the residence time for oxidation, with batch tests of much longer durations giving lower cyanide consumptions in gold recovery.

2.3.1. *Reasons for high cyanide consumption*

It had been originally suggested that high cyanide consumptions may be due to inefficient washing of the oxidized residue during solid/liquid separation and carry-over of soluble cyanicide ions, but this has been shown not to be the principal cause (Hackl and Jones, 1997). It has also been reasoned that cyanide consumption is related to the formation of iron and arsenic precipitates during bacterial oxidation and their subsequent carry-over to cyanidation.

Later studies showed that the major contributor to increased cyanide consumption is a result of reactive residual sulfur species in the bacterial-oxidation residue, which combine with cyanide to form thiocyanates (Hackl and Jones, 1997). The two forms of sulfur most likely to react with cyanide are polysulfides (S_x^{2-}) and thiosulfate ($S_2O_3^{2-}$), which react according to the following equations:

$$S_x^{2-} + CN^- \rightarrow S_{(x-1)}^{2-} + SCN^- \tag{1}$$

$$S_2O_3^{2-} + CN^- \rightarrow SO_3^{2-} + SCN^- \tag{2}$$

The more classical reaction in which elemental sulfur combines with cyanide to give thiocyanates is represented by

$$S^0 + CN^- \rightarrow SCN^- \tag{3}$$

Importantly, thiosulfate has been documented as the dominant initial species present in bacterial oxidation based on an attack of the pyrite surface by ferric iron *hexa*hydrate (Sand *et al.*, 1995). In this possibly more accurate portrayal of the oxidation mechanism, thiosulfate, and not elemental sulfur, is the first intermediate sulfur compound of predominance in a bacterial-oxidation system, according to

$$FeS_2 + Fe(H_2O)_6^{3+} + 3H_2O \rightarrow Fe^{2+} + S_2O_3^{2-} + Fe(H_2O)_6^{2+} + 6H^+ \qquad (4)$$

Irrespective of the first species of reaction, both thiosulfate and the polysulfide compounds (including elemental sulfur) should only be intermediary species in bacterial-oxidation processing. It is well accepted that soluble sulfates are expected to be the final species of bacterial-oxidation reactions and in this form sulfur is benign and not recognized as a cyanicide. As may be inferred by the above reaction, the total reaction pathway associated with bacterial oxidation is complex, resulting in conversion of sulfides into potential cyanicides and finally through to benign sulfates. Schippers *et al.* (1996, 2000) conducted some elegant research examining the mechanisms involved in the bacterial oxidation of sulfides, including pyrite. They include some detail on the reaction pathway for the conversion of the sulfide components into sulfates. Schippers *et al.* (1996) and Sand *et al.* (1995) proposed a cycle for pyrite degradation involving a number of transient sulfur species through a chain of reactions to the final soluble sulfate form. For the current discussion a simplified version might be illustrated as shown in Fig. 3.

Note that some of the intermediate reactions are reversible, and the occurrence of these cyanicides is influenced by reaction parameters such as pH, temperature, redox potential and ionic strength. In this chapter the authors have used the group term of *polysulfides* for all such unwanted intermediary sulfur species classed as cyanicides, including elemental sulfur (which is not unreasonable, given that all modifications of crystalline sulfur contain either rings or chains of sulfur atoms).

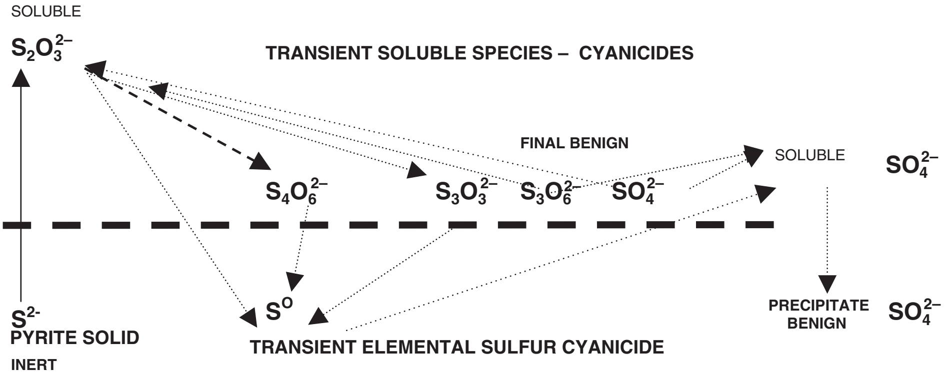

Fig. 3. Schematic cycle for pyrite degradation (adapted from Sand *et al.*, 1995).

2.3.2. Process concepts to reduce cyanide consumption

The motivation to examine concepts to reduce cyanide consumption was based on the reasoning that the cyanide consumption in the treatment of bacterial-oxidation residues should be remarkably low if the presence of polysulfides is minimized (Miller, 2000). In order to find practical solutions to minimize the presence of these species two basic principles were pursued:

1. *Process prevention*: If the rate of oxidation was improved or additional residence time allowed then this may prevent or reduce the presence of polysulfides in the oxidized residue. This might be achieved by:
   - small increases in residence time in bacterial oxidation to allow the conversion of polysulfides to proceed to benign sulfates;
   - the use of a finer grind size to improve the rate of oxidation and, hence, the conversion of polysulfides; and
   - the preferential removal of liquor during bacterial oxidation, which would lower the total ionic concentration of soluble species and remove initial polysulfides that had formed in the liquor. This would also improve the subsequent rate of oxidation and allow any accumulated polysulfides to be more readily converted into benign sulfates. Operating at a lower pulp density might appear to be an alternative to liquor removal. However, removal of liquor can allow more effective economic use of reactor oxidation capacity than operating at a lower pulp density, as modification to the operating pulp density can be performed during the liquor removal step.
2. *Process cure*: If polysulfide species were present in the final residue then an alternative is to examine possible methods to remove them before cyanidation. This might be achieved by:
   - the use of alkaline pre-aeration with lime to oxidize polysulfides;
   - the use of sodium carbonate for a similar duty; and
   - the use of flotation techniques to remove polysulfide components from the oxidized residue.

The residence time in the solid/liquid separation process after bacterial oxidation was also studied as this was noted as exerting an influence on polysulfide formation if efforts were not made to reduce polysulfide levels before solid/liquid separation.

2.3.3. Prevention and cure of polysulfide formation

A refractory gold concentrate with a relatively high sulfide content was used as feed material throughout the programme of work discussed below.

Table 3
Analysis of major species of refractory gold concentrate used for testwork

Fe (%)	As (%)	S (total) (%)	S^{2-} (%)	C (total) (%)	C (organic) (%)	Au (g/t)
31.4	6.8	31.3	31.1	3.83	2.94	52

This allowed for a direct comparison of results to be made between all tests and based on information presented in Table 2, a concentrate of high sulfide content was likely to encourage the presence of polysulfide cyanicides in the final residue. The composition of the concentrate, indicating the major elements present, is given in Table 3.

2.3.3.1. Polysulfide process prevention – influence of bacterial-oxidation residence time. Table 2 included results from comparative studies of gold extraction and cyanide consumption when treating residues from both batch and continuous bacterial-oxidation tests. As discussed earlier in this chapter, these results showed that lower cyanide consumptions are generally experienced for residues obtained from batch tests in comparison to those from continuous processing. This is presumed to be a result of the longer residence time associated with batch tests, which allows for oxidation of polysulfide cyanicides to benign sulfates.

In the first stage of testwork on the high-sulfide concentrate, both batch bacterial-oxidation tests and a continuous pilot-plant campaign were established and CIL gold-extraction tests performed on oxidized residues. A 5-day residence time and 15% pulp density with a feed sized at a P80 of $<75\,\mu m$ were used as the conditions for the piloting campaign, similar to what might be normal plant practice for treating this material. The continuous bacterial-oxidation piloting was conducted in a staged laboratory-reactor system with the capability of processing a few kilograms a day, and for this first campaign four stages of reactors were used, as would be associated with conventional plant. A minimum equivalent of three to four residence times was allowed for the system to reach steady state under continuous operating conditions before oxidized residues were taken for testing. Pulp samples taken from individual reactors were processed immediately for sulfur speciation analysis and gold recovery investigations; it is imperative to analyse and process samples immediately as labile sulfur species can be unstable with time.

The results of reagent consumptions and elemental sulfur analyses noted from CIL studies of residues obtained from both batch and continuous bacterial-oxidation testing are given in Table 4.

The objective for the CIL work was to maximize gold recovery while aiming to minimize reagent consumption. For the batch tests, the lower sulfur

Table 4
Reagent consumption and gold extraction from CIL tests from batch and continuous bacterial-oxidation residues

Residue Type	S^0 Content Post oxidation (%)	(%) NaCN in CIL	Carbon Concentration (g/L)	Time (h)	Gold Extraction (%)	NaCN Consumption (kg/t)	Lime Addition (kg/t)
Batch	<0.5	0.50	20	48	95	13	20
Continuous	2.0	0.25	20	48	93	38	60

Table 5
Sulfur speciation of reactor residue samples when adding a further secondary reactor in bacterial-oxidation piloting at feed P80 of 75-μm

	Primary Reactor[a]	First Secondary Reactor	Second Secondary Reactor	Third Secondary Reactor	Additional Secondary Reactor
Sequence	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5
Total sulfur (%)	25.3	21.2	13.2	9.0	4.6
Sulfide (%)	22.3	16.3	9.7	5.1	1.1
Sulfate (%)	0	2.5	1.7	2.0	2.3
Elemental S (%)	3.0	2.4	1.8	1.9	1.2

[a] Primary reactor was 3 × the volume of each secondary reactor and secondary reactors (all of equal volume).

content of the residue allowed a lower cyanide and lime consumption while achieving a higher gold recovery by using a higher cyanide strength. The reagent consumptions noted in treatment of the oxidized residues from the continuous plant were greater by a factor of 3, and gold recovery was reduced by ~2%. These findings support the results reported in Table 2, and suggest that this particular concentrate would produce an oxidized residue quite aggressive in downstream reagent consumption if it were to be treated by a conventional bacterial-oxidation plant.

This work did, however, provide the incentive to examine the effect of small increases in bacterial-oxidation residence time in a continuous pilot-plant system. This was achieved by the addition of a further secondary reactor to the continuous plant, creating a total of five stages of reactors. For the purpose of assessing the presence of cyanicides, elemental sulfur analysis was reasoned to be the most reliable analytical tool readily available and was used as a measure of the success of experimentation to reduce cyanicides. The results of sulfur speciation in residue samples taken from individual reactors for this second piloting campaign in which a fifth stage was added is given in Table 5.

It is evident from Table 5 that increasing the residence time by the addition of a single reactor stage gave significant reductions in elemental sulfur content of the final residue. The level of sulfur oxidation was also improved, as shown by the reduction in the sulfide content of the final residue, although it is accepted that an extension of residence time will result in additional expenditure. A brief economic review by the authors suggested that depending on the reductions achieved in reagent consumption and cyanide detoxification costs, these savings might be expected to pay for the additional capital expenditure in reactor tankage reasonably rapidly. However, while an extension of residence time appeared economically attractive, it was reasoned that if the other concepts of using a smaller particle size of feed or removal of liquor were beneficial in reducing cyanide consumption these may have the additional advantage of improving the rate of oxidation. The use of the additional reactor stage was therefore maintained for subsequent investigations to check this hypothesis. The results from these third and fourth piloting campaigns are discussed below.

2.3.3.2. Polysulfide process prevention – influence of feed particle size. While the issue of particle size and pulp density is recognized as an important parameter in determining the bacterial-oxidation kinetics of a concentrate (Bailey and Hansford, 1993), the majority of plants feed either an unground flotation concentrate or a concentrate that has been reground to remove the coarse sulfide particles produced in the flash flotation cell. The typical size of feed is therefore usually between a P80 of 45 and 63 μm with a top size limit of 120 μm. The first pilot-plant campaign discussed above had used a P80 of 75 μm.

Using this type of feed size in a bacterial-oxidation plant, it is reasonable to anticipate that an oxidation profile with respect to particle size will occur through the different stages of reactors, in which the smaller particles are oxidized more rapidly. In a practical sense for bacterial-oxidation plants, if an adequate transfer of oxygen can be provided, then a smaller feed particle size might be expected to give improvements in the rate of oxidation. Effectively this is achieved by increasing the availability of reaction sites by grinding, without interfering with other parameters. Potential improvements in reducing downstream cyanide consumption might also be realized based on the following reasoning.

An important reaction in a bacterial-oxidation circuit, which has already been described, is the reaction between pyrite and ferric iron, producing polysulfides. It is logical to believe that the conversion of polysulfides associated with the oxidation of larger particles will still be occurring in the final bacterial oxidation secondary reactor when the majority of smaller particles have been well oxidized. Larger particles should exert a higher demand for cyanide consumption due to the carry-over of the polysulfides associated with these particles into downstream processing. To test the concept of using a finer particle size of feed to reduce cyanide consumption while improving the oxidation rate, a new piloting campaign was initiated in which the feed was ground to a P80 of <20 μm. In practice, this could be achieved by the use of tower milling on a conventional plant. Table 6 gives a summary of the results from this work using sulfur speciation on residues taken from individual stages of reactors to assess the potential benefit of a smaller feed size.

Table 6
Sulfur speciation of reactor residue samples when using a concentrate at feed P80 of 20 μm

	Primary Reactor	First Secondary Reactor	Second Secondary Reactor	Third Secondary Reactor	Additional Secondary Reactor
Sequence	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5
Total sulfur (%)	21.8	10.2	4.2	1.6	1.1
Sulfide (%)	20.8	7.4	2.4	0.4	0.3
Sulfate (%)	0	1.8	1.1	0.8	0.5
Elemental S (%)	1.0	1.0	0.7	0.4	0.3

It is clear by comparing these results with those presented in Table 5 that using a finer feed size gives a considerable reduction in the concentration of sulfur in the final residue. The results also profile the progress of the oxidation through the reactor train and clearly indicate the benefits of using a reduced particle size on oxidation rate, with very low sulfide values being present in the final residue. The study also suggested that the previous benefits of the additional fifth reactor stage, representing an increase in residence time, may have been diminished by the use of a finer grind, as there are only marginal improvements in reducing the sulfur content of the final residue between the fourth and fifth reactor stage.

2.3.3.3. Polysulfide process prevention – bacterial-oxidation intermediate liquor removal. In the mid-1980s the belief was widely held that removal of bacterial-oxidation liquor after the initial primary stage of oxidation might be beneficial to oxidation rate and this step was a feature of some pilot-plant campaigns in these early years. It was reasoned that the removal of soluble ionic species such as ferric iron and arsenic and excess acid would reduce any potential inhibition of oxidation rate due to accumulation of these products. For the current work it was reasoned that achieving a higher rate of oxidation would improve the final residue characteristics prior to cyanidation by encouraging the conversion of polysulfides into benign sulfates. In addition to this, the intermediate removal of liquor would also remove much of the soluble polysulfide compounds that had formed in solution as initial oxidation reaction products.

Although further polysulfides would form after liquor removal, due to the oxidation of remaining sulfides, these should exert considerably less burden on the oxidation capacity of the bio-leach plant in their conversion into benign

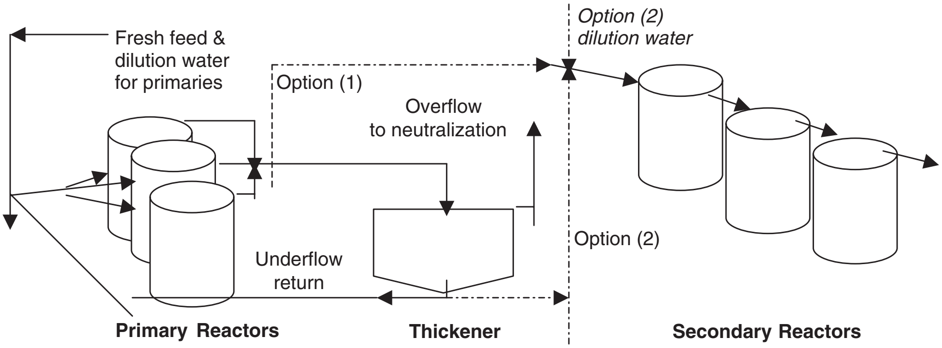

Fig. 4. Concepts of *liquor stripping* for bacterial-oxidation plants.

sulfates. In principle, preferential removal of liquor on a plant would be achieved by thickening of the partially oxidized product in closed circuit with the primary reactors and replacement of overflow liquor with fresh water.

Fig. 4 illustrates these alternative concepts as applied to a conventional bacterial-oxidation plant. Partially oxidized pulp acting as feed for the secondary reactors can either be taken as a direct bleed stream of overflow from the primary reactor (1), or re-diluted underflow from the thickening operation (2) can be used. Overflow containing the iron and arsenic values reports to neutralization in combination with the normal acidic effluent from the final solid/liquid separation operation.

As a relatively high mass loss also occurs in the primary reactors, this step gives an opportunity for the re-adjustment of pulp density, which would be beneficial in reducing the total reactor capacity needed, or increasing the residence time in the secondary reactors, the benefits of which have already been discussed.

This potential method of increasing oxidation rate has been termed *liquor stripping* by the current workers, and was used as part of this investigation to understand if this method would not only improve the oxidation rate but also encourage the conversion of polysulfides into benign sulfates. This concept was trialed, in which preferential liquor removal was achieved by using in-line filters located in the primary reactor of the pilot plant. Provision was made for fresh water make-up to the secondary reactor to re-adjust the pulp density of the partially oxidized solids for the subsequent oxidation stages. As the benefits of a finer particle size had already been demonstrated as being beneficial, the investigation of liquor stripping was performed in combination with the smaller feed size of a 20 μm P80.

Table 7 illustrates the results of sulfur speciation of samples taken from the individual reactors during this piloting campaign.

The beneficial effects of liquor stripping are quite evident by comparing these results with those in Tables 5 and 6, not only in terms of increased

Table 7
Sulfur speciation of reactor residue samples when using *liquor stripping* for bacterial oxidation at feed P80 of 20 μm

	Primary Reactor	First Secondary Reactor	Second Secondary Reactor	Third Secondary Reactor	Additional Secondary Reactor
Sequence	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5
Total sulfur (%)	22.3	9.2	3.4	1.0	0.9
Sulfide (%)	19.7	7.2	2.1	0.2	0.1
Sulfate (%)	2.5	1.3	0.7	0.5	0.7
Elemental S (%)	0.1	0.7	0.6	0.3	0.1

oxidation rate but also as reductions in elemental sulfur content. A feature of most significance is the considerable reduction in elemental sulfur even in the primary stage of reaction (0.1%) in comparison to the use of finer grinding alone (1%; Table 6), and conventional bacterial-oxidation processing (3%; Table 5). Moreover, Table 7 illustrates an increase in sulfur to 0.7% in the first secondary reactor, presumably owing to the action of further sulfide oxidation in this stage without liquor stripping. However, this was reduced by bacterial activity to 0.3% by the fourth stage and 0.1% by the fifth stage of processing.

Oxidized residue from the pilot plant was subjected to an extensive programme of CIL testing to determine the reductions in reagent consumption that might be expected as a result of these modifications to the bacterial-oxidation circuit. Table 8 compares the range of reagent consumptions and gold extractions noted during efforts to maximize gold extraction while minimizing reagent consumption when testing the residue.

It is evident that both cyanide and lime consumption have been decreased by a factor of 3 as a result of modifying the bacterial-oxidation process. Table 9 illustrates the differences in reagent consumptions between batch, conventional-continuous and modified-continuous residues for this material when converted to process consumptions both on a per tonne of concentrate and per tonne of ore basis.

Table 9 clearly illustrates the benefits in reducing reagent consumptions by applying a finer grind size and liquor removal as modifications to the bacterial-oxidation circuit. For a per tonne of ore basis cyanide consumption would be reduced from 3.3 to between 0.75 and 1.0 kg/t, while reductions in lime consumption from 5.4 to 1.3–1.8 kg/t could be anticipated.

2.3.3.4. Polysulfide process prevention – effect of solid/liquid separation after bacterial oxidation. During the course of the above study it was noted that the levels of labile sulfur species tend to increase with time following the exit

Table 8

Reagent consumptions and gold extraction from CIL testing of residues from pilot-plant incorporating liquor stripping on fine feed compared with conventional bacterial-oxidation processing

Liquor Stripping	Concentrate P80 (μm)	% NaCN in CIL	Carbon Concentration (g/L)	Time (h)	Gold Extraction (%)	NaCN Consumption (kg/t)	Lime Addition (kg/t)
Yes	20	0.35	20	48	95	6–12	15–20
No	75	0.25	20	48	93	38	60

Table 9

Reagent consumptions for gold extraction converted into kg/t of concentrate feed and ore, comparing batch bacterial-oxidation residues with those from normal continuous piloting operation and residues from a modified pilot-plant using liquor stripping and 20 μm feed size

Residue Type	Cyanide Consumption			Lime Addition		
	kg/t of oxidized residue	kg/t equivalent of flotation concentrate	kg/t equivalent of ore	kg/t of oxidized residue	kg/t equivalent of flotation concentrate	kg/t equivalent of ore
Batch	13	9	1.1	20	14	1.8
Continuous	38	26	3.3	60	42	5.4
Modified-continuous[a]	6–12	4–8	0.75–1.0	15–20	10–14	1.3–1.8

[a] *Liquor stripping* and feed P80 of 20 μm.

Table 10
Comparison of elemental sulfur in oxidized residue from final reactor with quantity present after 24 h in a simulated thickener

Sample No.	S^0 (%)	
	Reactor Residue	Thickener Underflow
1	1.1	3.3
2	1.5	2.5
3	1.2	2.8

of oxidized slurry from the bacterial-oxidation reactors. Table 10 shows the results from elemental sulfur analysis tests illustrating this phenomenon in which the elemental sulfur of some pulp residues taken from the last reactor are compared with the same pulp held in a thickening vessel for 24 h.

There was a substantial increase in the elemental sulfur content of residues taken from the 'thickener', as compared to residue taken from the last secondary reactor. Experiments were conducted to examine more closely the influence of time on this reaction and it was found that even when pulps taken from a reactor were allowed to stagnate for the relatively short period of 30 min, there was evidence of an increase in elemental sulfur content. On a plant, this effect would likely give rise to an increase in cyanide consumption as a result of the solid/liquid separation operation prior to cyanidation. It is believed that these differences in elemental sulfur content are a result of the different operating environment of the thickener in comparison to the reactor. The thickener is a quiescent non-aerated operation of lower temperature in comparison to the bacterial-oxidation reactor. Prior work concerning the stability of species responsible for elemental sulfur formation (Sand *et al.*, 1995; Schippers *et al.*, 1996, 2000) gives some credence to this reasoning. If transient sulfur species are allowed to be present at the end of bacterial oxidation then the thickening operation may further encourage the formation of elemental sulfur and, hence, higher cyanide consumption.

An example of this would be given by the following reaction, in which soluble thiosulfate is converted into insoluble elemental sulfur in a non-aerated acidic environment at lower temperature:

$$S_2O_3^{2-} + H^+ \rightarrow S^0 + HSO_3^- \quad (5)$$

Clearly, eliminating the presence of the polysulfide species in the first instance is highly desirable by ensuring their oxidation during bacterial oxidation and avoiding their presence in downstream processing. Some brief experimentation was made as part of this programme of work to examine the possibility of removing these cyanide-consuming species prior to cyanidation, as discussed below.

2.3.3.5. Polysulfide process cure – post-treatment of bacterial oxidation-residues to remove polysulfides prior to cyanidation. Hackl and Jones (1997) reported testwork that examined the alkaline pre-aeration of bacterial-oxidation residues with lime as a method for reducing or removing sulfur intermediates prior to cyanidation. The reaction of sulfur with lime, which gives soluble calcium polysulfides and thiosulfate, thereby removing potential cyanicides is given by

$$(2+2x)\mathrm{S} + 3\mathrm{Ca(OH)_2} \rightarrow 2\mathrm{CaS}_x + \mathrm{CaS_2O_3} + 3\mathrm{H_2O} \tag{6}$$

In dilute polysulfide solutions the value of x is predominantly unity and the objective of aeration is to oxidize the polysulfides and thiosulfate to sulfates. Hackl (1997) reported reductions in cyanide consumption by about half, while increasing lime consumption by a factor of approximately 2.5 times.

In an effort to investigate the potential of this technique further, some preliminary tests were conducted in the current work programme and while reductions in cyanide consumption were noted using lime pre-aeration, they were only of the order of a few per cent and not considered as significant. A further technique of alkaline pre-aeration was trialed using sodium carbonate, in which reaction of sulfur species to form soluble polysulfides and finally sulfates would be expected to occur; again, the reductions in cyanide consumption were found to be only a few per cent and therefore not of great significance.

A further technique of treating oxidized residues using flotation to remove the sulfur components was also tested. For the residue studied, this was found not to be selective enough to result in reductions in polysulfide compounds and, hence, cyanide consumption.

It is important to stress that none of these techniques were investigated in great detail and a larger programme of work is recommended by the authors to confirm the brief observations made here. It is, however, concluded that the *polysulfide process cure* approach of aiming to treat residues after oxidation in order to removed cyanicides gives much inferior results in comparison to the *polysulfide process prevention* approach, in which efforts are made to amend the cyanidation characteristics of the final residue by manipulation of the process conditions in the bacterial-oxidation process.

3. BRIEF COMPARISON OF BACTERIAL OXIDATION WITH PROCESS ALTERNATIVES

A number of alternatives to bacterial oxidation should also be considered for refractory gold concentrate treatment. Although treatment routes are project-specific, the following process routes are often included in studies, which should aim at examining the most appropriate process route for a project:

- On-site bacterial oxidation
- On-site pressure oxidation (see also Chapter 15)
- Roasting (see also Chapters 17 and 18)
- Fine grinding and direct leach
- Sale of concentrate to smelter
- Sale of concentrate to off-site bio-leach or pressure-leach plant

A brief summary of the major attributes of the alternative routes can be given as follows.

Pressure oxidation

- An effective and well-understood, proven method of oxidation, relying only on physical and chemical principles.
- Carbon is not oxidized or *blinded*, making the process less amenable to treating preg-robbing ores; acid pre-treatment is required for feeds high in carbonate.
- The higher capital and operating costs make the technique more suited to processing of concentrates with a gold-to-sulfur ratio high enough to support these costs.
- The high cost of purchase or lease of the oxygen plant is a notable expense; autoclaves are typically constructed from highly specialized materials.
- The high sophistication of operation with higher spares inventory is less well suited for less-developed regions of low skill base and maintenance capability.
- The technique is recognized as having low cyanide consumption in downstream gold recovery as complete conversion to sulfate is achieved but only with high-pressure/temperature oxidation.
- Low-pressure/temperature oxidation may give high sulfur formation and, hence, high cyanide consumptions under some conditions.
- The technique is often less flexible at managing fluctuations in concentrate composition through a project's life (*e.g.* sulfide value).

Roasting

- Often the only method for treatment of concentrates containing high quantities of organic carbon that are *preg-robbing* or encapsulate gold.
- Potential for production of saleable sulfuric acid product.
- Can be a low-cost method but highly dependent upon concentrate composition being treated; gaseous emission control is typically required.
- Can be a high-cost method if non-autogenous.

- The cost for gas scrubbing to remove elements such as arsenic often makes roasting the least cost-effective method of oxidation; arsenic stabilization can be very costly.
- New roasters are unlikely to be considered for many future projects due to increasing environmental concerns.

Fine grind and direct leach

- Although project dependent, there is often little improvement in recovery with grinding unless the gold in sulfides is larger than a few microns in size. The technique is not appropriate for recovering gold values in solid solution.
- Generally a relatively low capital cost.
- In some case, this option presents a low cost per tonne but a high cost per ounce of gold.

Sale of concentrate to smelter

- This option presents the lowest capital investment but there is a limited market for concentrates with high arsenic contents; it is more attractive for short-term projects of lower tonnage, which cannot justify capital expenditure.
- It is potentially easier to permit due to removal from site of toxic elements such as arsenic and no use of cyanide on-site.
- May have to 'tailor' a concentrate to a smelter's need, which may decrease gold recovery to concentrate.
- There is lower revenue due to smelter penalties (*e.g.* arsenic, mercury, bismuth) as well as smelting and transport costs.
- There may be delays in payment for gold contained in concentrate.

Sale of concentrate to off-site bio-leach or pressure-leach facility

- This is a relatively new concept for projects to treat concentrate off-site in an existing oxidation facility and is dependent upon spare capacity.
- The transport costs and treatment fee result in reduced revenues.
- The low capital investment makes it attractive for projects during the *start-up* phase or those with low tonnages of short duration, which cannot justify capital expenditure.
- Potentially easier to permit due to removal from site of toxic elements such as arsenic and no use of cyanide on site (as for smelting).

4. CONCLUSIONS

Reagent consumption is a major consideration in the design and operation of any bacterial-oxidation plant. The results presented here have suggested that in order to achieve reductions in cyanide consumption particularly when treating high sulfide grade concentrates, one or more of the following modifications should be incorporated into the bacterial-oxidation process:

1. The preferential removal of process liquor during bacterial oxidation (*liquor stripping*), which reduces the concentration of soluble elements present in the final pulp.
2. A finer particle size of feed to the bacterial-oxidation process.
3. Small extensions to the residence time of the bacterial-oxidation process.

A desktop study by the authors indicated that a 20 μm P80 grind using tower milling might be both practical and economical. The potential reduction in cyanide consumption and detoxification costs while improving the rate of oxidation should be a substantial driver in improving the cost effectiveness of bacterial oxidation.

A further desktop study suggested that considerable savings would occur by using *liquor stripping* without a reduction in feed size. When used in combination with a finer particle size the contribution of benefits to improve cost effectiveness should be further compounded. Liquor stripping and a finer feed size offer the potential to reduce cyanide consumption while improving the oxidation rate and, if ultra-fine grinding were to be considered this may also result in marginal improvements in final gold recovery for some projects by exposure of siliceous gold. For these reasons, the authors would recommend the use of these two techniques in combination rather than extensions in residence time.

5. RECOMMENDATIONS FOR FUTURE AREAS OF INVESTIGATION

Many of the results presented here were derived from commercially orientated piloting investigations operated to obtain project-specific design criteria for feasibility studies. While this gave the opportunity to examine the influences that modifications to the bacterial-oxidation process can have on reducing cyanide consumption and improving oxidation rate, the tests by no means have been exhaustive and there is room for much further work.

Three potential areas for future work are considered to be of value:

1. Investigating the benefits of *ultra-fine grinding* to give an even finer feed size.
2. A more detailed investigation into *post-oxidation treatment techniques* to minimize cyanide consumption.
3. A more detailed investigation of the use of *liquor stripping* to manage reactor oxidation-capacity more effectively by achieving intermediate

adjustments in pulp density and removal of soluble species as the oxidation progresses.

The reasons why these areas are considered worthy of further investigation is as follows:

5.1. Ultra-fine grinding

The authors believe that significant further improvements in bacterial oxidation performance could be achieved by ultra-fine grinding the feed to the bacterial-oxidation circuit. Preliminary results have shown a substantial improvement in kinetics and a further reduction in cyanide consumption for a feed P80 of 6 μm, compared to a 20 μm feed size; overall gold recovery was also a little higher for a 6 μm feed, possibly due to liberation of fine gold occluded in silica. Ultra-fine grinding has been recognized as a requirement for bio-leaching of chalcopyrite concentrates and significant work has been performed to successfully integrate ultra-fine grinding into copper bio-leach processing at demonstration scale (Rhodes, 2003). With the development of relatively cheap and efficient ultra-fine grinding mills, the authors believe that this together with liquor stripping could produce further significant process improvements together with the potential to marginally increase final gold recovery.

5.2. Post-treatment techniques

Preliminary work was carried out to test the postulation that bacterial-oxidation product contains unstable oxy-sulfur compounds that are reduced to cyanide-consuming polysulfides in the non-oxidizing environment. Several tests were carried out on pulp as it was discharged from the bacterial-oxidation circuit using pure oxygen and hydrogen peroxide in an effort to oxidize these components. These preliminary results indicated a potential reduction in cyanide consumption and it is thought that these strong oxidizing agents enabled the rapid oxidation of the unstable oxy-sulfur complexes to stable sulfates. The oxygen/hydrogen peroxide requirement appeared to be small and given the probable rapid kinetics, only a relatively small reaction vessel should be required. It is considered that further work in this area is justified.

5.3. Liquor stripping to enable operation at a higher pulp density

Bacterial-oxidation plants are currently operated at relatively low pulp densities normally in the range 10–20% solids; this together with the relatively long residence time has resulted in large reactors being required, particularly for large tonnage operations. Such reactors represent a significant cost component due to their size. The authors believe that the low-density requirement is driven at least partially by the need to keep the ionic concentrations of ferric and arsenic at level that do not significantly affect bacterial activity and thus the process kinetics. The use of liquor stripping to control the concentration of ferric ion and arsenic in the bacterial-oxidation reactors should thus allow for operation at a higher relative density with significant capital and operating cost savings. Factors such as oxygen uptake rate and heat removal kinetics would have to be taken into consideration but it is believed that significant potential savings are possible.

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Mike D. Adams (Editor)

Chapter 17

Roasting developments – especially oxygenated roasting

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The roasting of ores and concentrates can be defined as the heating of a material to cause reaction and the expelling of volatile matter without causing fusion. Oxidative roasting is used extensively to pre-treat base and precious metal-bearing materials and to oxidize iron sulfides to generate sulfur dioxide for fixation with lime or sulfuric acid production. Roasting reactions are generally in the range of 450–820°C, and most typically around 550°C.

For the recovery of gold from refractory ores and concentrates, roasting has been used extensively for decades. For severe refractory gold ores, it was the exclusive pre-treatment process and accordingly, its development is presented in detail, finishing with the most recent technology, oxygenated roasting for whole ores.

Commercially, four important steps have been witnessed in the development of roaster equipment:

- Rotary kiln and multiple hearths (*e.g.* Edwards)
- Fluidized bed (*e.g.* DORR-Oliver)
- Circulating fluidized bed (CFB) (*e.g.* Inco and Lurgi)
- Oxygenated fluidized bed (*e.g.* Independence and Goldstrike)

Table 1 summarizes the advantages and disadvantages of each process. Thereafter general comments are given on each process type.

The development of new technologies was driven by increased throughput requirements, improving efficiencies, reducing costs and increasing environmental concerns.

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Table 1
Roaster performance comparison (adapted from Maycock *et al.*, 1990)

Parameter	Edwards	Fluids	CFB	Oxygenated
Relative throughput per unit area	Very low	Moderate	High	High
Gas/solids mixing	Poor	Good	Very good	Good
Bed temperature control	Poor	Good	Very good	Good
Control of gas composition	Limited	Good	Very good	Very good
Solids retention time	Fixed	Fixed	Variable	Fixed
Feed type (wet or dry)	Dry	Both	Both	Both
Roast whole ore	No	Possible	Yes	Yes
Treat arsenic ore	Concentrate	Yes	Not yet	Not yet
Development	Pre-1910	1940s	1960s	1980s

Fluidized-bed roasters took over from multiple-hearth roasters when relatively large throughputs were required. A typical example of this was Giant Yellowknife Mines Limited, Yellowknife, Canada (Thomas, 1985). In 1954, Giant Yellowknife experimented with the expansion of production from 36 t/d concentrate to 120 t/d. The Edwards multiple hearth occupied 350 m^2 for 36 t/d; the fluidized-bed roaster eventually commissioned in 1958 required a two-stage roaster with one bed 4 m in diameter followed by the second stage 3 m in diameter (total 19 m^2) for 120 t/d. This was a significant improvement in tonnes per unit area and operated successfully until the late 1990s.

The early roasters were installed with the minimum of gas cleaning. As time progressed, units such as Cottrell precipitators, to remove dust, baghouses, to remove arsenic trioxide (as shown in Fig. 1), and the capturing of sulfur dioxide gas by neutralization with lime or the production of sulfuric acid were also integrated into roaster plants.

CFB roasters are similar to fluidized-bed roasters but significantly improve gas/solids mixing, bed temperature control and throughput per unit area. This is achieved with the use of cyclones in conjunction with the roaster. CFB roasters are now being used with enriched-oxygen atmospheres, which further improves throughput per unit area and reduces the size of gas-cleaning equipment, thereby reducing capital costs.

Oxygenated roasting in fluidized beds also improves throughput per unit area as well as reducing the size of gas-cleaning equipment. Independence Mining Company, Nevada, USA (Kosich, 1992) has three units in operation and Barrick Goldstrike, Nevada, USA also has two units in operation (Cole *et al.*, 1999).

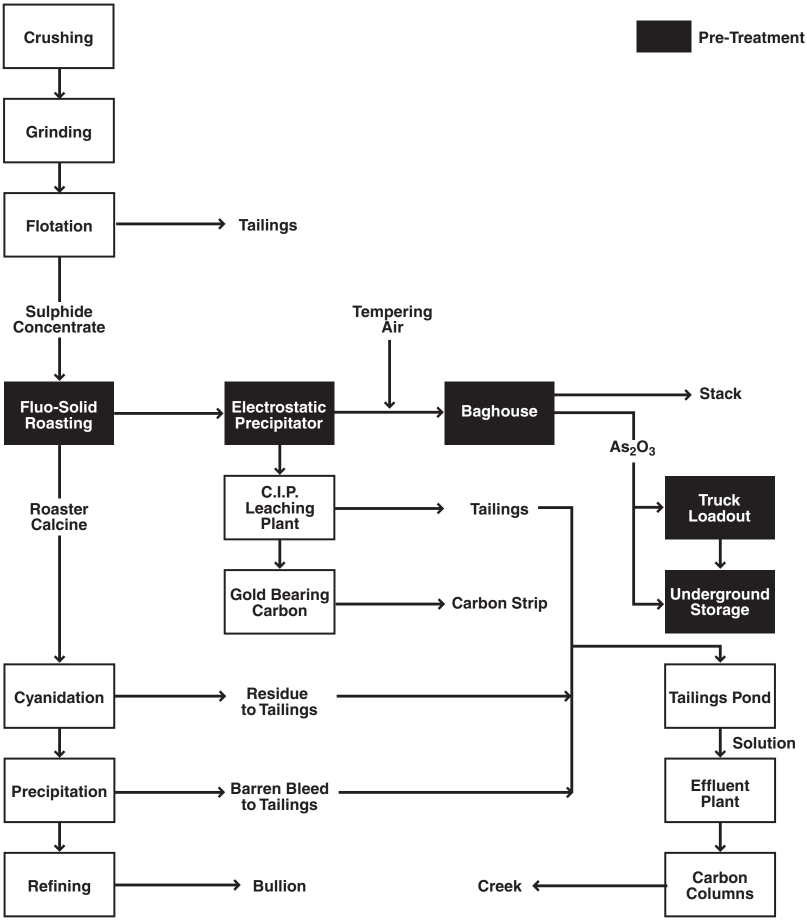

Fig. 1. Simplified mill and roaster flowsheet (Giant Yellowknife Mines Limited, Canada).

1. RABBLE ROASTERS

Before the 1940s, rotary kilns and multiple-hearth roasters were used for the treatment of refractory ores. The most common in the gold industry was the single Edwards roaster as it provided better bed temperature control. The roaster consists of an enclosed hearth, brick lined and up to 40 m long and 3.6 m wide (Maycock *et al*., 1990). Concentrate is advanced down the hearth by rotating rabble arms. A cross-section of a rabble roaster is shown in Fig. 2.

There are several examples of the successful application of the Edwards roaster to gold extraction: to name a few, Giant Yellowknife Mines Limited (Thomas, 1985), Ashanti Goldfields Corporation (Ghana) Limited and the Government Roasting Plant in Zimbabwe (Goode, 1993).

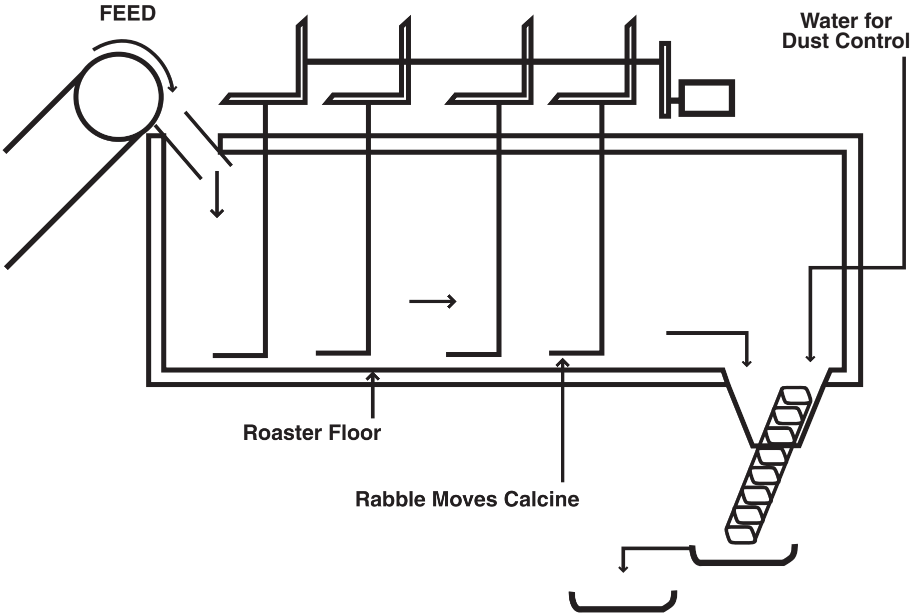

Fig. 2. Diagrammatic view of a rabbled hearth roaster.

2. FLUIDIZED-BED ROASTERS

There is a variety of flowsheets using fluidized-bed roasters but of the more successful and older operation is Giant Yellowknife Mines Ltd., Yellowknife, Northwest Territories, Canada (Maycock *et al.*, 1990). The circuit can easily be understood by reviewing the flowsheet depicted in Fig. 1. Roasting of a bulk arsenopyrite concentrate is done in two stages: the first stage having partial oxidizing conditions to volatilize the arsenic at 500°C and the second stage, also at 500°C, is an almost complete oxidizing roast to oxidize sulfur and provide a porous calcine that is amenable to cyanidation. Both stages are autogenous, obtaining fuel from the sulfur in the concentrate. A cross-section of a fluidized-bed roaster is shown in Fig. 3. Off-gases are cleaned of gold-bearing dust in an electrostatic precipitator; thereafter the gold is recovered by carbon-in-pulp. The cleaned arsenic-trioxide fume is cooled and the relatively pure dust collected in baghouses at 105°C for shipment to wood-preservative manufacturers or stored in underground vaults within the permafrost. Gold recovery is typically between 87 and 92%.

Two-stage roasters are used for arsenopyrite ores and one-stage roasters for pyritic ores. The reason for the two-stage roasters can be understood by studying the process chemistry. Ideally, the calcine product from roasters should be chocolate brown in colour. This is achieved by producing a calcine

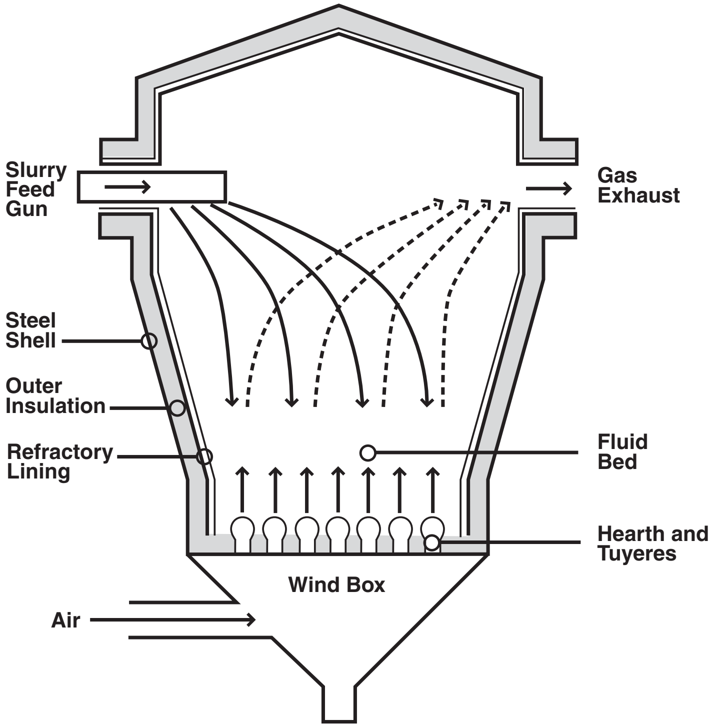

Fig. 3. Diagrammatic view of a fluid-bed roaster.

containing approximately 80% hematite [Fe_2O_3] and 20% magnetite [Fe_3O_4]. This indicates that complete or close to complete sulfide oxidation has been achieved:

$$3FeS_2 + 8O_2 \rightarrow Fe_3O_4 + 6SO_2 \tag{1}$$

$$3FeS + 5O_2 \rightarrow Fe_3O_4 + 3SO_2 \tag{2}$$

$$4Fe_3O_4 + O_2 \rightarrow 6Fe_2O_3 \tag{3}$$

Two-stage roasters that treat arsenopyrite ores are more complex. Initially, the arsenic is volatilized, diffusing through the expanded, heated arsenopyrite lattice and thereafter a mixture of hematite and magnetite is produced:

$$FeAsS \rightarrow FeS + As \tag{4}$$

$$3FeS + 5O_2 \rightarrow Fe_3O_4 + 3SO_2 \tag{5}$$

$$4Fe_3O_4 + O_2 \rightarrow 6Fe_2O_3 \tag{6}$$

The volatilized arsenic is oxidized immediately to arsenic trioxide in the presence of oxygen:

$$4As + 3O_2 \rightarrow 2As_2O_3 \tag{7}$$

The production of arsenic pentoxide (As_2O_5) is to be avoided as a reaction between hematite and arsenic pentoxide occurs, forming a non-porous ferric arsenate which tends to occlude the gold in the calcine and reduce subsequent gold recovery by cyanidation:

$$Fe_2O_3 + As_2O_5 \rightarrow 2FeAsO_4 \tag{8}$$

Formation of ferric arsenate is avoided by roasting in a deficient oxygen atmosphere in the first stage of a two-stage roaster installation. For environmental stability, ferric arsenate is a desirable product. This conflict of required products does not occur in pressure-oxidation processing.

One of the major disadvantages to roasting is the presence of high antimony in the ore. Levels above 0.5% antimony in the Giant Yellowknife concentrate feed to the roaster could cause clinkering and an expensive shutdown for roaster-bed clean-out. The reason is related to the mineral stibnite [Sb_2S_3], which readily oxidizes to antimony trioxide, which causes clinkering of the concentrate because of its low melting point (Thomas, 1988):

$$2Sb_2S_3 + 9O_2 \rightarrow 2Sb_2O_3 + 6SO_2 \tag{9}$$

Hence, at the Giant Yellowknife operation, a tight control was required on the sulfide and antimony analyses, a typical concentrate analysis being Au – 57 g/t; S – 20%; Sb – 0.3%; As – 9%. The content of sulfide sulfur has to be above 15% to ensure autogenous roasting of the wet concentrate.

Besides Giant Yellowknife, there are many other operations worldwide, which have been adequately covered in the literature (Maycock *et al.*, 1990; Marsden and House, 1992).

The chemistry of roaster technology detailed in this section is generally applicable to other roaster technologies for gold extraction.

3. CIRCULATING FLUIDIZED-BED (CFB) ROASTERS

In the 1960s Lurgi, together with Vereinigte Aluminiumwerke A.G. in Germany (Peinemann, 1991), developed the CFB technology for the alumina industry. This technology was applied to many other commercial applications for both exothermic and endothermic processes:

- calcination of clay and phosphate rock;
- combustion of solid fuel for power plants;

- oxidation of refractory gold ores and concentrates; and
- dry cleaning of waste gases.

Also in the late 1950s and early 1960s, Inco and Falconbridge respectively, initiated commercial processing of pyrrhotite to recover iron, nickel, copper and cobalt using CFB technology. For every tonne of calcine carried out through the production outlet, 6 t are recirculated. The circulating load provides long residence time for the coarser fraction to ensure sulfur elimination. Eventually, the coarser particles are abraded to smaller sizes and leave the roaster (Boldt, 1967).

As shown in the Cortez operation schematic in Fig. 4, refractory gold ore or concentrate is fed to the circulating fluid-bed roaster, which is roasted with air or oxygen-enriched air, introduced through a nozzle grate at the bottom of the roaster. A portion of the hot calcine collected by the cyclone is recycled to the roaster. The rest of the calcine goes forward for gold recovery by cyanidation.

Several advantages are claimed for the CFB technology (Peinemann, 1991):

- reduced capital and operating costs;
- good process control;
- excellent sulfur and carbon burnout;

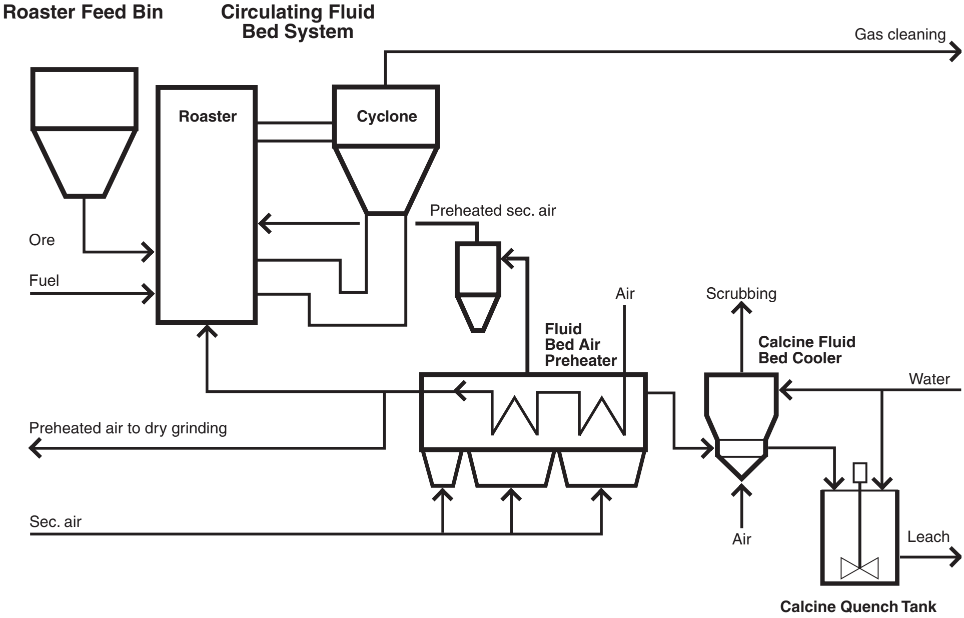

Fig. 4. CFB roasting plant for gold-bearing whole ore.

- excellent turndown of throughput; and
- acceptance of wide feed particle size (1–1700 μm).

Lurgi CFB technology was used in a single roaster at Cortez (NV, USA) (now decommissioned), and is used for two parallel units installed by Newmont (NV, USA). The Cortez operation treated 1,820 t/d of ore containing 1.1% sulfide sulfur, 1.1% organic carbon and 2.9% carbonate carbon (Peinemann, 1991).

CFB technology is discussed in more detail in Chapter 18.

4. OXYGENATED ROASTERS

Several Carlin Trend ores and other deposits in Nevada are associated with sulfides and carbonaceous matter. Some types of carbonaceous material have the ability to *preg-rob* gold in the cyanidation stage. Accordingly, not only does the sulfide material need to be oxidized but also the carbonaceous matter has to be destroyed or made inert. One drawback of pressure oxidation is that carbonaceous matter is neither destroyed nor made inert. Hence, the fluidized-bed technology using oxygen has been developed successfully as an alternative for whole-ore treatment.

The air roasting of concentrates that are refractory because of their high sulfide content has been successful because the process is exothermic at sulfide sulfur concentrations in excess of 15% owing to the heat released on oxidizing the sulfides. This process is exothermic in the presence of air. Roasting of whole ores with sulfide sulfur content of 1–3% requires fuel, as there is insufficient heat from the oxidizing of the sulfides. The added expense of fuel was one of the reasons why whole-ore air roasting was not previously developed. Also, sulfide sulfur is roasted at temperatures below 650°C. Above this temperature over-roasting occurs, causing reduced recoveries by cyanidation. Unfortunately, carbon is difficult to burn at temperatures below 730°C. Balancing of these two requirements has been difficult to achieve with existing air-injected fluidized-bed roasters, without compromising gold recovery.

Thus, a need existed in the industry to treat whole ores that were not only sulfidic, but also carbonaceous and could also operate at a temperature low enough to give satisfactory gold recovery.

In 1985 (Kosich, 1991), Freeport McMoran Inc. (New Orleans, LA, USA), started developing an oxygenated roaster for treating a sulfidic/carbonaceous whole-ore deposit in Nevada. The result was a patent (Smith *et al.*, 1990) and the successful commissioning of three oxygenated roasters with a total capacity of approximately 4,500 t/d at their Nevada properties.

In 2000, Barrick Goldstrike commissioned an oxygen-roasting circuit using dry grinding and Freeport McMoran Inc. oxygenated-roasting technology. A detailed description is given in the following Section.

5. OXYGENATED ROASTING

5.1. Introduction

Two fluid-bed roasters were constructed in 1999 to pre-treat carbonaceous/sulfidic refractory ores at Barrick Goldstrike Mines Inc., (NV, USA). These are the largest gold-ore roasters in the world, using almost pure oxygen to remove contained organic carbon and sulfide sulfur prior to a conventional carbon-in-leach (CIL) process for gold extraction. This section describes the overall roasting process as well as the design features based on a successful operating facility. At Barrick Goldstrike the carbonaceous matter or organic carbon is referred to as total carbonaceous matter (TCM).

Indications in the early 1990s were that ore reserves were becoming increasingly carbonaceous, besides being sulfidic, at the Barrick Goldstrike Mines operations. This led to reviews of alternative pre-treatment technologies to autoclaving, which was used to treat refractory sulfidic ores at the property. These carbonaceous ores are called *double refractory*, because the gold is locked within sulfide minerals and the carbonaceous matter adsorbs gold during conventional cyanide leaching (Chryssoulis and Cabri, 1990). Pressure oxidation (autoclave leaching) would not overcome the preg-robbing characteristic of carbonaceous material, which would significantly hurt gold recoveries. The carbonaceous ores were mined starting in late 1999, and comprised a reserve of approximately 80 million t with an average grade of 5 g/t. An alternative pre-treatment had to be determined to maintain annual gold production at about 2 million ounces.

Studies concluded that whole-ore roasting was the best-proven technology at the time. Other pre-treatment options were discounted if they were inherently unsuitable to the Goldstrike ores or had not received significant commercial applications. Different roasting options were therefore considered, including Lurgi's CFB (Folland and Peinemann, 1989) and Freeport-McMoRan's oxygen-enriched roasting (Smith *et al.*, 1990). Based on extensive testwork, oxygen-enriched roasting was selected for pre-treatment owing to its ability to achieve high gold recoveries from the Goldstrike ores. This technology was also well proven in commercial operation (Brittan, 1995), with two plants operating since 1989 at Jerritt Canyon and Big Springs (now decommissioned).

By mid-1997, a preliminary process flowsheet, shown in Fig. 5, was defined.

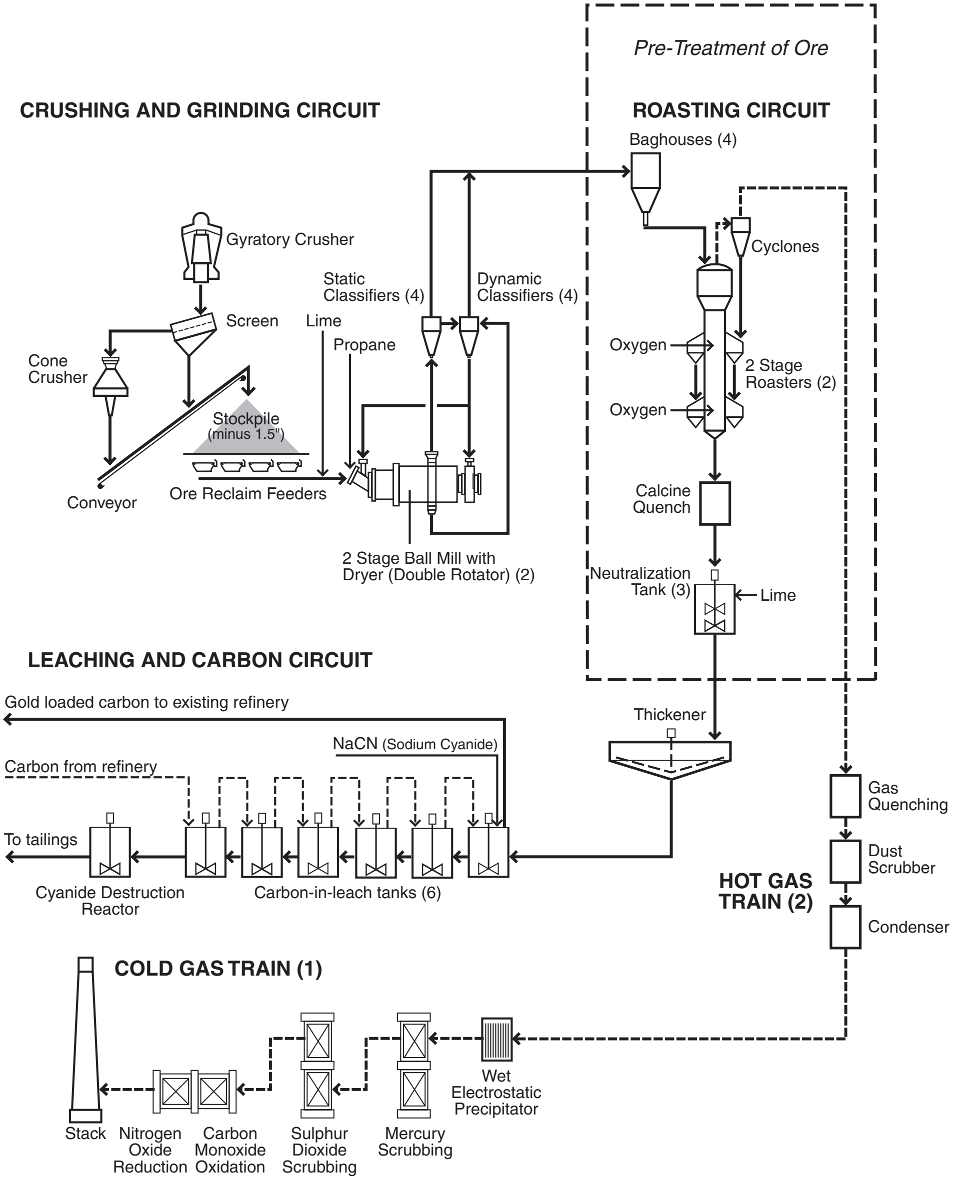

Fig. 5. Oxygenated roaster flowsheet.

Detail engineering was based on the following unit operations for pre-treatment of carbonaceous ore reserves at an average rate of 11,000 t/d:

- Primary and secondary crushing run-of-mine ore to obtain 80% passing 1.9 cm.

- Dry grinding of crushed ore using two double-rotator mills to obtain 80% passing 74 μm.
- Whole-ore roasting of ground ore using two two-stage, oxygen roasters to remove contained organic carbon and sulfide sulfur by oxidation.
- Two gas-quench and dust-scrubbing systems, one for each roaster, including off-gas condensers and mist eliminators.
- One common gas-cleaning train, including electrostatic precipitation and removal of mercury, SO_2, CO and NO_x,
- Conventional CIL process for gold extraction from the roasted ore.

5.2. Ore mineralogy

The majority of the carbonaceous ore reserves at the Barrick Goldstrike property are in distinct zones within the footprint of the Betze-Post pit. The remainder of this ore comes from underground, primarily the Rodeo and Griffen deposits and to a lesser extent Barrick's Meikle mine.

The mineralization is generally within a Devonian Popovich formation. The host rock is typically decalcified muddy limestone and silicified sedimentary breccias. The gold is mainly present as colloidal gold occluded in the arsenian pyrite [FeS_2] and marcasite [FeS_2], so the gold concentration generally increases in the fine-grained sulfide minerals. There are also trace amounts of orpiment [As_2S_3], realgar [AsS], stibnite [Sb_2S_3], arsenopyrite [FeAsS] and cinnabar [HgS] present in the deposit. Sulfide sulfur concentrations vary from 0.5% to 3.5% throughout the reserves and approximate to a grade of 2.0% overall.

There is significant variation in the carbonate content throughout the reserves. For the first few years of processing, the carbonate concentration was about 5%, which is near the historical Betze-Post level. A significant increase is projected as mining progresses to the west of the Betze-Post pit, where carbonate values are anticipated in the range from 15% to 20%.

Organic carbon content in the ore ranges from 0.5% to 4% and averaging about 1.5%. Tests conducted on the carbonaceous material indicate that the ore is strongly preg-robbing as defined by standard preg-rob and Barrick Goldstrike Mines Inc. (BGMI) bleach leach procedures (see also Chapter 38). Further mineralogical evaluations found that the strongly carbonaceous matter is highly amorphous and generally has a small crystalline structure. All the carbonaceous materials analysed from Goldstrike ores are comparable to anthracite or higher-grade coal.

5.3. Roaster chemistry

Various chemical reactions occur in the roaster, including:

1. Combustion of organic carbon
2. Combustion of carbon monoxide

3. Combustion of sulfide sulfur
4. Fixation of sulfide dioxide with ore, lime and hematite
5. Reaction of lime with carbon dioxide
6. Dehydration of ore
7. Vapourization of mercury
8. Oxidation of nitrogen.

These reactions are described in more detail below. Based on chemical analyses of the reactants and products in pilot and commercial-scale tests, this process chemistry provides an adequate model for mass and energy balances of the roasting process to design the roaster and off-gas cleaning equipment (Warnica *et al.*, 2002).

Combustion of organic carbon. Carbon from all sources (ore, coal and oil) oxidizes within the roaster fluid beds to carbon monoxide and carbon dioxide with a resulting split between CO and CO_2 estimated at 4% and 96% (percent carbon by weight). Carbon monoxide may oxide further in the roaster freeboard to reduce CO levels in the off-gas. The carbon reactions occur as follows:

$$2C\ (s) + O_2\ (g) \rightarrow 2CO\ (g) \tag{10}$$

$$2CO\ (g) + O_2\ (g) \rightarrow 2CO_2\ (g) \tag{11}$$

The overall extent of organic carbon oxidation in the ore is estimated to range from 81% to 89%, depending on the ore mineralogy. The extents of coal and diesel-oil oxidation are approximately 99.5% and 100% overall, if applicable. Carbon monoxide remaining in the roaster off-gas is removed by a CO incinerator.

Combustion of sulfide sulfur. Oxidation of orpiment [As_2S_3], realgar [AsS] and arsenopyrite [FeAsS] proceed simultaneously until they are fully reacted. Due to the highly oxidizing environment, essentially all of the arsenic is converted into solid ferric arsenate ($FeAsO_4$) or arsenic pentoxide (As_2O_5), which report to the calcine:

$$FeAsS\ (s) + 3O_2\ (g) \rightarrow FeAsO_4\ (s) + SO_2\ (g) \tag{12}$$

$$2As_2S_3\ (s) + 11O_2\ (g) \rightarrow 2As_2O_5\ (s) + 6SO_2\ (g) \tag{13}$$

$$2As_2S_2\ (s) + 9O_2\ (g) \rightarrow 2As_2O_5\ (s) + 4SO_2\ (g) \tag{14}$$

$$4FeS_2\ (s) + 2As_2O_5\ (s) + 11O_2\ (g) \rightarrow 4FeAsO_4\ (s) + 8SO_2\ (g) \tag{15}$$

Decomposition and partial oxidation of pyrite [FeS_2] proceeds to pyrrhotite [Fe_7S_8], most of which is further oxidized to hematite [Fe_2O_3]:

$$7FeS_2\ (s) + 6O_2\ (g) \rightarrow Fe_7S_8\ (s) + 6SO_2\ (g) \qquad (16)$$

$$4Fe_7S_8\ (s) + 53O_2\ (g) \rightarrow 14Fe_2O_3\ (s) + 32SO_2\ (g) \qquad (17)$$

The overall extent of sulfide combustion is estimated at 99%, with 97.5% reacting in the first-stage bed and 1.5% in the second-stage bed.

Fixation of sulfur dioxide. Sulfur dioxide is fixed by reactions with minerals in the ore (carbonates and hematite) and with the lime added to the ore prior to dry grinding. Based on pilot test results, sulfur dioxide fixation ranges from 54.5% to 89.5% by reaction with the ore minerals. The lime addition rate is controlled at 50% of the stoichiometric requirement for the remaining sulfur dioxide, with a lime utilization of 60%. Therefore, the lime fixes 30% of the sulfur dioxide remaining after reaction with ore minerals. The total sulfur dioxide fixation in the roaster is estimated to range from 68.1% to 92.7%, depending on the carbonate content of the ore.

Sulfur dioxide reacts with carbonate and hematite in the ore:

$$2CaCO_3\ (s) + 2SO_2\ (g) + O_2\ (g) \rightarrow 2CaSO_4\ (s) + 2CO_2\ (s) \qquad (18)$$

$$2Fe_2O_3\ (s) + 6SO_2\ (g) + 3O_2\ (g) \rightarrow 2Fe_2(SO_4)_3\ (s) \qquad (19)$$

Additional SO_2 fixation is by reaction with lime added to the ore:

$$2CaO\ (s) + 2SO_2\ (g) + O_2\ (g) \rightarrow 2CaSO_4\ (s) \qquad (20)$$

Sulfur dioxide remaining in the roaster off-gas is removed by the gas-cleaning system and SO_2 scrubber, which has an overall removal efficiency of 99.95%.

Reaction of lime with carbon dioxide. Ten percent of the lime is estimated to react with carbon dioxide:

$$CaO\ (s) + CO_2\ (g) \rightarrow CaCO_3\ (s) \qquad (21)$$

Dehydration of ore. The dehydration of clays or other hydrated minerals occurs predominantly in the first-stage bed as evaporation of water to superheated vapour. Moisture in the roaster feed ore and water vapour in air additions is also superheated.

Vaporization of mercury. All of the mercury in the feed ore vaporizes to elemental mercury in the roaster off-gas, and is removed by the gas-cleaning system.

Oxidation of nitrogen. Nitrogen is thought to be oxidized in the roaster with a 9:1 volumetric ratio of NO to NO_2:

$$N_2\ (g) + O_2\ (g) \rightarrow 2NO\ (g) \tag{22}$$

$$2NO\ (g) + O_2\ (g) \rightarrow 2NO_2\ (g) \tag{23}$$

Although there is usually little conversion of atmospheric nitrogen to NO_x at temperatures below 980°C (1,800°F), the presence of NO_x in the off-gas may be due to feed nitrogen or the high partial pressure of oxygen.

5.4. Dry grinding

Because the gold-encapsulating sulfides are extremely fine-grained there was no economic opportunity for flotation upgrade and whole-ore oxygenated roasting was determined to be the appropriate method, preceded by dry grinding (Thomas *et al*., 2001).

The ore contains about 2.0% sulfide sulfur and about 1.5% TCM (contained organic carbon) with calculated blended heat values between 0.45 and 0.70 kJ/t (200 and 300 BTU/lb). This is insufficient to evaporate any moisture in the roaster feed and dry grinding was chosen accordingly.

Four processes are widely used for dry grinding of rock and these were evaluated for the Goldstrike roasting plant. Table 2 identifies examples and some limitations of each.

The choice of double-rotator mills was deemed to have the least risk. Two 7,500 kW mills were chosen to enhance roaster availability and assure more

Table 2
Dry grind process options

Description	Examples	Limitations
Tertiary crushing followed by ball milling	AngloGold's Jerritt Canyon, Elko, NV, USA	High moisture and clay concerns in tertiary crushing. Dust control issues in crushing
Semi-autogenous milling followed by ball milling	Newmont's Mina Hasa, Indonesia	Too large a scale-up factor for Barrick
Secondary crushing followed by double-rotator milling	Newmont's Mill #6, Elko, Nevada, USA	Structural concerns in double-rotator internal diaphragms. Otherwise acceptable
Vertical roller mills followed by ball milling	Cement plants throughout the world	Extreme hardness and abrasiveness of the Goldstrike ore

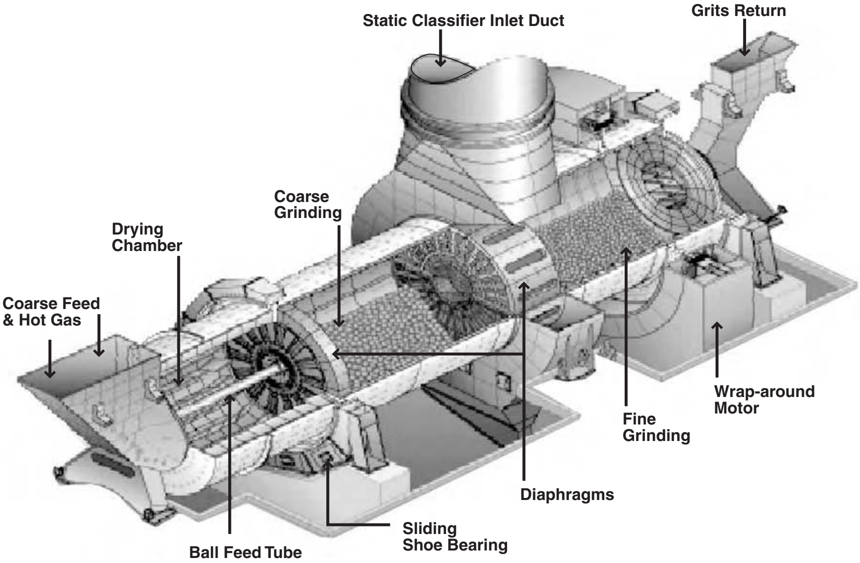

Fig. 6. Pictorial of dry-grinding mill.

flexibility for ore-hardness variations. A cutaway sketch of the dry-grinding mill is shown in Fig. 6.

5.5. Roaster operation

The roasting process is accomplished in two parallel circuits to heat carbonaceous refractory gold ores and oxidize the contained organic carbon and sulfide sulfur. As shown in Fig. 7, each roaster is comprised of two bubbling, fluid-bed reactors in a single vessel with an average design capacity of 5,550 t/d. This equipment includes a fluidized feed-system, first and second-stage cyclone systems, and ancillary systems. The following description refers to one of the roaster circuits. Key process parameters are established from extensive testwork on Goldstrike ores (Warnica *et al.*, 2002).

As shown by the process flow diagram in Fig. 5, the fluidized feeder distributes ore continuously from its hopper to the first-stage (upper) bed of the roaster. The feeder is fluidized with air and overflows into the roaster through standpipes extending into the first-stage bed. The roaster feed ore is 80% passing 74 μm. Up to 30% of the ground ore is smaller than 10 μm, depending on the extent of particle agglomeration.

The upper bed is maintained at constant temperature in the range from 525°C to 595°C. The heat source for the first stage is provided by the ore's net heat of reaction. Coal may be added to the ground ore to provide additional heating for low fuel-value ores, or fresh water may be injected to cool the

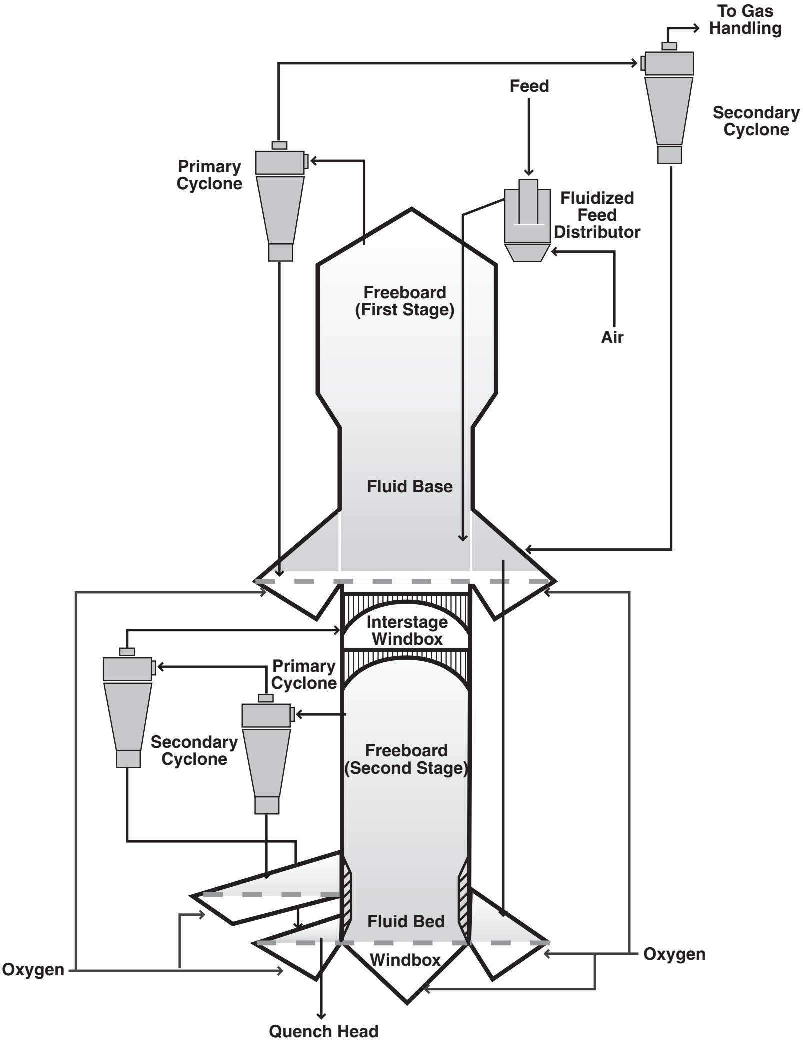

Fig. 7. Roaster vessel flow diagram.

first-stage bed for high fuel-value ores. Water may also be sprayed into the first-stage freeboard to cool the roaster off-gas, if excessive freeboard combustion occurs. The ore is oxidized predominantly in the first stage.

Solids discharge continuously from the first stage through the inter-stage solids transfer system to the second-stage (lower) bed, which is maintained at a constant temperature in the range from 525°C to 620°C. If heating is required, diesel oil is injected through oil guns around the bed circumference. Water may be added with the diesel oil to reduce flame temperatures and sintering, in amounts up to 75% relative volume. Oxidation is essentially completed in the second stage. The overall oxidation is typically 99% for sulfide sulfur and 88.5% for organic carbon.

Solid product discharges by gravity from the second-stage bed to the calcine quench system.

Low-pressure, high-purity oxygen (99.5%, (v/v)) is introduced as the fluidizing medium through the cold windbox to the second-stage bed and the solids transfer boxes. Hot exhaust gases from the second-stage reactor are conveyed through the inter-stage gas transfer system and the hot windbox to fluidize the first-stage bed. The hot, oxygen-rich gas from the second stage promotes rapid oxidation of the organic carbon, sulfur and fuel in the first-stage bed. The first-stage exhaust gases are de-dusted in the gas discharge system before passing to the gas quench and cleaning train.

The exhaust gas from each roaster stage is de-dusted in a set of high-efficiency, primary and secondary cyclones. In each stage of the roaster, a coarse fraction of elutriated solids is recovered by two primary cyclones and returned to the bed. A fine fraction is recovered by two secondary cyclones and fed forward through the reactors, to reduce accumulation of fines within the roaster. Fines from the first stage are therefore fed forward to the second stage, and fines from the second stage are fed forward to the calcine product.

Dust is carried over to the roaster off-gas cleaning circuit from the first-stage cyclone separators. The off-gas system is designed to process dust in amounts up to 4.5% of the dry ore feed, but the actual amount is much less in practice and depends on the off-gas rate. Dust collected within the roaster area is recovered in the roaster dust collection baghouse and returned to the roaster feed distribution box. Cleaned air is emitted to the atmosphere through the roaster baghouse stack.

The ore fuel value is correlated with the contained organic carbon (%TCM) and sulfide sulfur (%S) as follows:

$$\text{Ore Fuel Values [BTU/lb]} \rightarrow 120 \times \%\text{TCM} + 72.6 \times \%\text{S} \tag{24}$$

where, units of composition are per cent of dry weight.

The total oxygen plant supply is limited to 1,000 t/d for two roasters, so the maximum ore rate decreases with increasing fuel value and hence oxidant requirement. The total ore rate for two roasters is an average rate assuming 90% operating availability.

The retention limit (36 min) corresponds to a bed inventory of 190 t in one roaster, which is the combined inventory of both stages. This minimum retention time is established by testwork to yield the desired gold recovery.

The coal rate for first-stage heating is only required in a few years with low ore fuel values. Water is injected for bed cooling in the other years with higher fuel-value ores. The autogenous limit (0.53 kJ/t (225 BTU/lb)) is what separates these operating regimes.

The roasters can process a wide range of ore compositions at the desired average rate (11,000 t/d), corresponding to the dry-grinding capacity. The oxygen plant has some excess capacity for most of the ore feeds, except very high fuel-value ores that may require additional bulk oxygen (LOX) to supplement the plant oxygen supply.

The first-stage (upper) reactor temperature is maintained at 550°C by either coal addition or water injection. The water rate increases with the ore fuel value, so there are corresponding increases in gas volumes and velocities. Operating conditions of the second-stage (lower) reactor are relatively uniform, regardless of fuel value. The temperature of lower reactor is nominally increased to 565°C by oil injection, but may be allowed to float. The actual operating temperatures of both stages depend on characteristics of the feed ore and its amenability to cyanide leaching.

In general, the project philosophy was to use proven technology and equipment where possible to avoid custom engineering and unpleasant surprises during start-up. It was also a project standard to install spare mechanical equipment and avoid unnecessary roaster shutdowns for routine maintenance. These criteria had implications for equipment selection and flowsheet development. For example, unsupported refractory domes were limited to the typical maximum diameter that has demonstrated operational experience and long-term campaigns (6.71 m). Also, installed spare equipment was supplied for most blowers, and all pumps and solids transfer systems. The only exceptions were the start-up and preheat air blowers, which are used infrequently and can be tested off-line.

The roasters themselves are custom-designed by virtue of the specific process objectives and their size. Key features of the process are:

- Fluid-bed roasting using almost pure oxygen as the process gas.
- Two roasting stages in a single vessel to ensure a high level of both organic carbon and sulfide sulfur oxidation.

The Goldstrike roasters are the largest of their kind, with freestanding vessels about 33.5 m high and a refractory dome diameter of 6.71 m. Their sheer size is evidence of the level of custom engineering that was required for process, mechanical, and structural engineering.

5.6. Process design basis – roaster

The process design basis incorporates many aspects, but only a few are presented to reveal some of the main considerations for equipment selection and sizing.

The base-case ore composition was assumed to have

- 1.9% sulfides as S;
- 1.2% organic carbon as C; and
- 5.5% carbonates as CO_3,

with a fuel value of 0.65 kJ/t (282 BTU/lb). This composition represented an average feed for the first few years of operation. The corresponding reactions were modelled using the roaster chemistry to yield a mass and energy balance of the system, which was generally used for sizing the vessel and other equipment. The oxygen plant supply was to be 1,000 t/d for two roasters, with a purity of 99.5% (v/v). The process was to be controlled so the concentration of oxygen in the off-gas is not less than 10% (wet basis).

A special design case was also used to represent the maximum velocities and temperatures expected in the first-stage freeboard, for sizing this part of the vessel and the off-gas system. The maximum velocities were assumed to occur for a theoretical ore composition with the maximum concentrations of organic carbon and sulfide sulfur, not necessarily for the same year of the mine plan. The corresponding ore fuel value was 0.7 kJ/t (302 BTU/lb). The maximum temperature was selected at 760°C to account for possible combustion of carbon monoxide in the first-stage freeboard.

One of the main constraints on roaster size is the diameter of the self-supported refractory domes that form the top and bottom of the hot windbox. These domes are subject to a combination of loads due to weight, differential pressure, and thermal expansion. The inside diameter of 6.71 m is based on inherent mechanical limitations and operational experience from other processes. Although larger domes have been constructed, the selected size has demonstrated long-term reliability. This diameter determines the size at the bottom of the first-stage bed and the second-stage freeboard. Gas velocities in the fluid beds and freeboards determine other diameters.

A maximum superficial velocity of 0.46 m/s determines the diameter of the first-stage freeboard, using the special design case with a high fuel-value ore for gas volumes. This maximum velocity keeps dust carry over within acceptable levels for the off-gas system. The resulting freeboard diameter is 10.8 m. Two conical sections provide transitions from the hot windbox. One of these transitions is gradual over the bed height of 4.0 m, and the other is more abrupt in the lower freeboard.

A minimum fluidization velocity of 0.21 m/s or mechanical limits of the refractory domes determine the diameter at the bottom of the beds. Bed velocities may be somewhat higher than the minimum fluidization value, depending on the ore composition, but they remain within accepted limits of bubbling fluid beds. The diameter at the bottom of the second-stage bed is

Table 3
Roaster internal dimensions

Vessel location	Internal dimension (m)
First-stage diameters	
Freeboard	10.82
Bed top	8.38
Bed bottom	6.71
Second-stage diameters	
Freeboard	6.71
Bed top	6.71
Bed bottom	5.79
First-stage heights	
Freeboard	6.40
Bed	3.96
Second-stage heights	
Freeboard	6.17
Bed	5.18

5.8 m, and one conical section provides a gradual transition over the bed height of 5.2 m.

The internal dimensions of the roasters are summarized in Table 3, where freeboard heights are determined by the transport disengaging height of elutriated solids. External dimensions depend on the total refractory and shell thickness that is approximately 36 cm.

Solids feed and distribution system. Based on other plant experience, multiple feed chutes are used to improve operations and product quality. Splitting a high-solids feed rate into several equal streams presents a challenge. The *fluoseal* feed distributor aerates the solids, and overflow weirs yield uniform distribution to each of six feed chutes. This device has been used successfully for many calcining and roasting applications. The feed chutes extend into the first-stage (upper) fluid bed, to maintain a pressure seal and avoid venting hot roaster gases to the dust-collection system of the feed distributor. Feed chutes are vented to the roaster freeboard to avoid solids slugging and to maintain constant flow. The internal support arrangement of the feed legs allows thermal expansion in a dust-laden environment, using lateral braces with guides on the vessel shell.

Solids-transfer systems. In general, the solids flow easily when aerated, but not after being stagnant during shutdown periods. An almost vertical angle of repose is evidence of this undesirable behaviour of stagnant solids. All solids-transfer chutes are therefore vertical, except very short runs from the fluoseal feeder to the feed legs. These angled runs do not pose transfer problems, however, because solids entering these pipes are generally well aerated and the pipes are never filled with stagnant solids. Purge air is introduced at critical locations such as the cone valves, which are used to control bed levels.

Fluidized transfer boxes are used exclusively to convey solids between chutes and fluid beds. Transfer boxes on the Goldstrike roasters are the largest ever built, due to the large difference between freeboard and bed diameters. All transfer boxes are hung from spring hangers for additional support that accommodates thermal expansion of the vessel. Thorough fluidization of the transfer boxes is an important aspect to aerate the solids and maintain flow, especially in regions below the incoming chutes.

First-stage gas distribution and hot windbox. Hot exhaust gases from the second-stage freeboard are conveyed to the hot windbox that separates the first- and second-stage reactors. The hot windbox is formed by the space between the two self-supporting refractory domes. Gas enters the side of this windbox and flows upwards through 701 tuyères to fluidize the first-stage bed. Although the gas is cleaned to some extent by primary and secondary cyclones, fine particulate solids are unavoidable, resulting in long-term maintenance requirements of either solids build-up (scaling) or erosion of the tuyère holes. Tuyères are designed to minimize these possibilities, by using relatively large vertical holes to reduce gas velocity and pressure drop. Based on test experience, the hole size is selected to allow solids bridging and avoid draining the bed during shutdowns. During normal operation, the tuyère holes gradually plug due to scaling, which is removed during periodic maintenance shutdowns. Tuyère plugging is detected by increased pressure drop.

Aspirators. Particulate solids that enter the hot windbox with the gas stream and by sifting through the first-stage tuyères are removed continuously during normal operation by aspirators. Twenty-four holes are distributed over the bottom refractory dome of the hot windbox, between the hot windbox and the second-stage reactor. Using principles of fluid induction, medium-pressure oxygen is injected through each hole by an aspirator to induce gas flow and purge solids from the windbox. The design of these aspirators is based on experience with phosphate calciners. The removal of solids from the hot windbox significantly reduces the maintenance requirements due to tuyère scaling and erosion.

First-state water injection. Water guns are located around the bed circumference at two elevations. Twelve guns at the higher elevation are generally used during normal operation with full bed levels. Six guns at the lower elevation are used only during start up when the bed level is low. Water is injected typically into the splash zone near the top of a fluid bed, where there is intimate contact with solids circulating between the bed and freeboard but water vapour does not increase bed velocities.

Second-stage oil injection. Depending on the desired temperature, the second-stage bed may be heated by injecting an emulsion of diesel oil and water through oil guns located around the circumference. Diesel oil is supplied evenly to each of 16 oil guns by positive-displacement pumps with multiple heads. Water is then mixed with the oil by an in-line mixer located just upstream of each oil gun. Water can be added in amounts up to 75% (v/v) to reduce flame temperatures as required, depending on operational experience and gold recovery. Air from the purge air blower conveys the oil and water emulsion into the bed, and keeps oil guns clear of solids when not being used. Air is also used to cool the oil guns.

Freeboard water sprays. Six atomization nozzles are installed in the roof of the first-stage freeboard, to spray water and protect the roaster and off-gas system from high temperatures due to possible combustion of carbon monoxide. Fresh water is delivered by a high-pressure turbine pump, as required at rates up to 1.4 m^3/h. Different numbers of nozzles admit water, depending on the freeboard temperature. This type of system has been used for numerous fluid-bed reactors, primarily for incineration applications.

Start-up air system. The roasters are normally operated using high-purity oxygen, but started up using air. One multistage centrifugal blower is connected to both roasters, and isolated as required to start one roaster at a time. There is a smooth transition from start-up air to oxygen as the desired bed temperatures and levels are achieved.

Preheat burner system. Two preheat burners are mounted on the second-stage freeboard to heat a shallow first-stage bed above its autoignition temperature. Preheat equipment is used only for cold starts or after extended shutdowns. Ore is introduced and bed levels are increased after the desired temperature is achieved. Each burner is rated at 2,930 kW. One multistage centrifugal blower is connected to both roasters, and isolated as required to start one roaster at a time. The preheat burner blower supplies 100% excess air to two burners.

Purge air-blower system. Air is injected into the roasters at various locations to

- fluidize the feed system;
- provide the transport medium for diesel oil and water injection;
- cool oil guns; and
- purge solids from instruments and other equipment.

Three positive displacements purge air blowers are used for this air supply. One blower provides the air requirements of each roaster, and an additional blower is connected as an installed spare to provide continuous operation during blower maintenance. Each blower has a capacity of 1,200 N m^3/h, which is small in comparison with the oxygen supply.

The feed ore is oxidized predominantly in the first stage, and the remaining fuel value is only sufficient to offset some heat losses from the second stage and the sensible heating of the fluidizing oxygen. Since gold recovery may be enhanced by heating the second stage to a higher temperature than the first, instead of letting it float, two options were considered to heat the second-stage bed: preheating the fluidizing oxygen and direct fuel-injection. Oxygen preheating was dismissed to avoid the increased capital cost and engineering complexity of adding heat exchangers and replacing steel gas distributors with refractory domes, because oxygen temperatures greater than 315°C would have been required. Direct fuel injection was therefore selected, but special considerations were given to reduce flame temperatures and avoid sintering the bed, which is thought to occur at bed temperatures above 650°C. Provisions were made to inject an emulsion of diesel oil and water, which can control second-stage bed temperatures over the desired range from 525°C to 620°C and reduce the tendency for sintering.

5.7. Process design basis – roaster off-gas cleaning

The roaster off-gas system quenches the hot off-gas and then processes it for removal of particulate solids, mercury, SO_2, CO and NO_x. The two roaster gas systems are kept separate through particulate collection and are then tied together. Because of the very high dust loads, it was felt that attempting to combine the two systems prior to dust removal would compromise the reliability of the process.

Particulate removal. Particulate collection is achieved by multiple stages of wet cleaning. Given that roaster calcine is handled wet and strong SO_2 is present in the off-gas, a dry system was never a consideration. Gases are first cooled to saturation and partially cleaned in an open quench tower. The vessel consists of an open vertical chamber with a series of hydraulically atomized spray nozzles followed by a disengagement tank to separate the gas and entrained water/particulate. Because of the very large particulate loadings entering the quencher, it was prudent to use a fully open, low-velocity vessel to minimize problems associated with build-up and erosion. The arrangement of the vessel suits the roaster plant layout and minimizes the handling of hot, heavily loaded gas. Special attention was required at the interface between the hot gas and wet quencher to prevent the heavy build-up and rapid corrosion that often occurs here.

About 90% of the incoming particulate is collected in the quencher. Removing the bulk of the particulate, especially the coarse fraction, in the low-energy quench stage is important to minimize problems with the subsequent scrubbing stage. After reviewing the options with respect to scrubbing equipment, a variable throat venturi was selected. The scrubber operates at 40″ wg and includes alumina tiles to protect against erosion. Scrubbing water is introduced through open-bore pipes, enabling partial recirculation of the water. The key reasons for selection of the venturi are the absence of internal components, which are prone to build-up and erosion, and its well-proven performance.

The gases leaving the scrubbing stages are saturated at 130–160°C. A gas-cooling step was required for a number of reasons:

- The gas temperature had to be reduced to about 80°C to enable subsequent mercury collection (a vapour-pressure issue).
- Cooling the gas resulted in substantial amounts of water being condensed. Collecting the water here enabled it to be reused, while minimizing water-balance problems in downstream gas-absorption systems.
- Condensation of the water reduced the actual flow of gas substantially, along with the size of downstream fans and ductwork.

Numerous equipment options were available including open spray chambers, packed or tray towers, and shell and tube-type coolers. Two-stage cooling was also considered. A single shell and tube-type condenser was selected. The decisive reason for this was mercury; a significant portion of the metallic mercury present in the gas was expected to condense as the gas was cooled to 80°C. The single shell and tube-type condenser did not require a ‘dirty’ heat exchanger to cool contact water with the potential for mercury accumulation. Fouling of the tubes was the main concern during the design stage but has not been a problem due to the effective gas cleaning upstream and the large volumes of condensate providing continuous washing of the heat-transfer surfaces.

Water condensed at the cooler is returned to the quenching/scrubbing stage. The quencher removes the bulk of the particulates, including the coarser fractions and uses spray nozzles, so particulate-free water is used. With the bulk of the particulate removed and the absence of spray nozzles, recirculation is used at the venturi. However, the solids content of the circuit is kept below 5% (w/w). This circuit has enabled reliable operation while minimizing water usage and the subsequent impact on overall water balance.

At this point in the system, the gas is cold, essentially particulate-free and could be handled reliably without concerns over build-up. The two roaster systems were, therefore, combined to minimize project cost. A booster fan was included for each roaster to facilitate draft/flow control and reduce the draft in downstream equipment. The fans were selected with a fan speed as low as practical (1,800 rpm) to maximize reliability. Chevron-type mist eliminators are included upstream of each fan to collect condensate that forms in the duct runs. This minimizes the amount of condensate to be drained via the fan casings.

The combined roaster gases are then cleaned in a wet electrostatic precipitator (wet ESP). Wet ESPs are efficient collection devices for very fine particulate and mist, and play a key role in all metallurgical acid plants. The wet ESP was not part of the original flowsheet but was included to serve several functions:

- Complete collection of particulate.
- Collect fine condensed forms of mercury and mercury compounds.
- Remove acid mist (SO_3 and H_2SO_4), which would cause opacity problems at the stack.

A two-compartment wet ESP was installed, enabling automated washing with power off. Fogging nozzles were installed to ensure a continuous film of water is always present on the collecting electrodes. The particulate/mist collected in the wet ESP is bled from the gas-cleaning circuit.

Mercury removal. Mercury removal is then completed by scrubbing with mercuric chloride, $HgCl_2$ (Boliden-Norzinc process). The process is well established in base-metal smelters but collects only vapour-phase, metallic mercury, so it is important to collect other forms in the upstream equipment. Mercury is absorbed by the recirculating solution as follows:

$$HgCl_2\ (aq) + Hg\ (v) \rightarrow Hg_2Cl_2\ (s) \tag{25}$$

The solid mercurous chloride (Hg_2Cl_2) is separated in settling cones. A portion of the collected solid is bottled in special flasks, which is then shipped to mercury producers. The remainder is chlorinated with Cl_2 gas to regenerate $HgCl_2$ for return to the scrubber. The absorption tower is a packed column with two levels of mesh pads for mist elimination. This was required to minimize mercury emissions as a result of mist losses and the associated dissolved and suspended mercury compounds. All the mercury-handling equipment was installed in a separate building to isolate mercury from the rest of the process equipment. A provision was also made for installation of an electrolytic cell to produce metallic mercury as product while regenerating the chlorine gas.

Sulfur dioxide removal. The next unit operation is SO_2 scrubbing. Selection of SO_2 removal technologies is always difficult because of the large number of available processes. A concentrated-mode, dual-alkali scrubbing process was selected for the following key reasons:

- Sulfuric acid production was considered but dismissed on the basis of the small tonnage of acid, the wide range of sulfur contents in the ore, and the impact this variability would have on plant operation. In particular, the need to keep the SO_2 concentration above its autothermal point would result in the acid plant driving the roaster.

- The high concentrations of SO_2 (2–10% on a dry basis), together with the high collection requirements, necessitated a solution-based scrubber. Direct lime or limestone processes are not suitable for these process conditions.
- A concentrated-mode, dual-alkali process using soda ash and lime is well suited for the process conditions and performance requirements. It offers the benefits of solution scrubbing while using lower-cost lime as the key reagent.

The system selected is as follows:

SO_2 is scrubbed from the gas in a seven-tray plate tower. Absorption occurs in a recirculating stream of sodium salts:

$$Na_2SO_3 + SO_2 + H_2O \rightarrow 2NaHSO_3 \tag{26}$$

A bleed stream is regenerated using a slurry of slaked lime:

$$Ca(OH)_2 + 2NaHSO_3 \rightarrow Na_2SO_3 + CaSO_3 \cdot \tfrac{1}{2}H_2O + \tfrac{3}{2}H_2O \tag{27}$$

The regenerated sodium sulfide is separated from the precipitated solids and returned to the scrubber.

Two regeneration reactors are included to enable pH adjustment and particle growth. The precipitated calcium sulfide is separated in a thickener and pumped to tailings while thickener overflow is returned to the scrubber. The regeneration system was designed to operate with gravity flow to simplify its operation and maximize reliability. Sodium make-up is provided in the form of a soda-ash solution. A novel feature of the system is the absence of a filter; since the gas entering the SO_2 scrubber is water-saturated, the system has almost no evaporative capacity. As a result, the system water-balance forced a bleed stream to be provided – thickener underflow was used for this. While there are some sodium losses attributable to this, they are minor in comparison to the simplification and improved reliability associated with elimination of the filter.

The final unit operations are for CO and NO_x, both requiring elevated operating temperatures. The main fan was located prior to these steps, which enabled a smaller fan to be installed due to the lower temperature and corresponding lower actual flow rate. Again, a relatively slow speed (1,800 rpm) was selected to maximize reliability. The weak CO and any trace hydrocarbons are destroyed in a recuperative thermal oxidizer. Incoming gas is preheated in a shell and tube heat-exchanger using combustion-chamber exhaust gases. It then enters the combustion chamber where a burner increases temperature to about 815°C. The gas leaves through the heat exchanger at a controlled temperature of about 340°C, in preparation for NO_x reduction. An ammonia-based selective catalytic-reduction unit (SCR) using a zeolite catalyst was installed. Aqueous ammonia is injected ahead of the catalyst and reacts with the NO_x compounds. SCR is a well-proven technology and, most importantly for this application, the zeolite catalysts are very resistant to poisoning by heavy metals. This is not the case for the metal-oxide catalysts used for CO and hydrocarbon oxidation and is the fundamental reason that a catalytic approach was not considered for the oxidizer.

The roaster gases start off at a very high elevation, so the system was laid out to take advantage of this. The gases are moved downward through the particulate-cleaning stage, eliminating horizontal duct runs that are prone to build-up. Fans were located at grades where they could be readily serviced.

Gas-cleaning performance. The gas-cleaning system has exceeded design criteria, as shown in Table 4.

Roaster performance. Goldstrike's roasting facility began operation in March 2000; Table 5 shows plant throughput and availability performance since start-up.

The commissioning and start-up of the facility proceeded smoothly. For ease of construction and commissioning the start-up of each mill/roaster train was separated by 1 month. This proved to be advantageous for the

Table 4
Performance of roaster-gas system

Component	Design throughput (kg/h)		Actual outlet throughput (kg/h)	
	Inlet	Outlet	2000	2001
Particulate	22,680	2.7	2.0	0.9
Mercury	18	0.09	0.01	0.03
SO_2	9,072	20.4	7.3	6.4
CO	544	21.4	2.7	12.0
NO_x	54	16.7	6.7	6.5

Table 5
Barrick roaster throughput

Year	Throughput (Mt/year)	Throughput (t/h)	Availability (%)
2000	2.82	376	85.4
2001	4.28	563	86.8
2002	5.31	665	91.2
2003	5.36	694	88.1

start-up of the second train in that design deficiencies were corrected prior to going hot. Design capacity for the first train was achieved 2 weeks after start-up, while the second train reached design capacity within hours of start-up (Wickens *et al.*, 2003).

Facilty performance has improved significantly since commissioning. Design plant throughput was 11,000 t/d and current plant throughput ranges between 14,500 and 15,500 t/d. The grinding circuit has benefited from the following initiatives:

- reducing ore feed size;
- maintaining consistent coarse chamber ball-charge levels;
- using real time kWh/t to maximize energy efficiency; and
- using smaller make-up ball sizes in both chambers.

The increase in production with the roasters is primarily associated with a trade-off between fuel value (BTU/lb ore) and processing rate and to a lesser extent minor plant modifications around the ore feed system. The roasters were designed to treat a base case heat value (282 BTU/lb ore (0.65 kJ/t) at 253 t/h) for a set amount of oxygen. Instantaneous processing rates have increased by leveraging the roasters capacity to treat a given BTU per unit of time. Given the ability to blend for fuel value, the average fuel value currently being fed to the roasters is in the range of 235 BTU/lb ore (0.55 kJ/t).

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Chapter 18

Roasting of gold ore in the circulating fluidized-bed technology

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Lurgi Metallurgie GmbH, since 2002 part of Outokumpu Technology (OT) and recently renamed to Outokumpu Technology GmbH, has progressively developed the principle of fluidized-bed reactor systems in several different forms over a period of almost 50 years for a multitude of process applications. The versatility of the fluidized-bed reactor system has manifested itself in the treatment of minerals including solid fuels and for metallurgical processes both in the ferrous and non-ferrous fields. Process applications have included roasting, calcining, combustion and charring of coals, as well as off-gas treatment. Oxygenated roasting technologies are dealt with in Chapter 17.

1. HISTORY OF GOLD-ORE CIRCULATING FLUID-BED ROASTING TECHNOLOGY

In the course of its development of various forms of fluidized-bed roasting technology Lurgi (now Outokumpu Technology) commercially introduced the advantages of circulating fluidized-bed (CFB) technology to the industry. Prior to this roasters mainly employed the stationary fluidized-bed process.

The CFB technology was originally developed for the alumina industry in the mid-1960s by Lurgi in cooperation with Vereinigte Aluminium Werke

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Table 1
Outokumpu roasting technology for concentrates and whole ore

Year	Location	Number and kind of plant	Type of ore
1969	Goldfields, South Africa	2 Stationary fluid bed	Concentrate
1975	Anglo American, Welkom, South Africa	2 Stationary fluid bed	Concentrate
1975	Anglo American, Ergo, South Africa	3 Stationary fluid bed	Concentrate
1987	KCGM, Gidji, W.A.	1 Circulating fluid bed	Concentrate
1989	KCGM, Gidji, W.A.	1 Circulating fluid bed	Concentrate
1990	Placer Dome, Cortez, Nevada	1 Circulating fluid bed	Run of mine ore
1992	Newmont Gold Company, Nevada	2 Circulating fluid bed	Run of mine ore
1994	Minahasa, Indonesia	1 Circulating fluid bed	Run of mine ore

(VAW) (now Norsk Hydro ASA). Owing to the significantly lower operating costs and easier process control, the technology soon became popular in the alumina industry and Lurgi has since supplied dozens of CFB calciners to the alumina industry worldwide. During the past 15 years the CFB technology has been successfully applied to roasting refractory gold ores and concentrates (see Table 1). Suitability of the CFB technology for this application has been demonstrated on many occasions in CFB pilot plants and also in commercial CFB roasting plants.

The first commercial application of CFB roasting systems was installed at KCGM's Gidji roaster (Australia) for gold concentrates. Further CFB roasters followed at Cortez (Nevada, USA), Newmont (Nevada, USA) and Minahasa (Indonesia) for refractory whole ores. The small plant sizes compared to stationary fluidized bed roasters reduced the investment costs and the excellent temperature control within a narrow operation window improved gold recovery considerably.

2. THEORETICAL BACKGROUND OF ROASTING

It is known that in fluidized reactor systems, particle concentrations can reach several hundred kilograms per cubic metre of fluidization gas. This high solid concentration results in large contact areas between oxidation gas and solids. Excellent conditions for enhanced heat and mass transfer are thus provided, supporting nearly "ideal" isothermal conditions and good reaction kinetics. The mechanism is further improved when the difference between particle and gas velocity, the *slip velocity*, is high.

2.1. Categories of fluidization reaction systems

The different conditions of gas velocities and solid concentrations allow the classification of fluidization reaction systems into four categories:

2.1.1. The 'Classical' bubbling fluidized bed or stationary fluidized bed

- The gas velocity is moderate ($u = 0.4$–$1.5\,\mathrm{m/s}$).
- There is a distinct transition between a high solid's concentration volume (the *bed* with a clearly defined surface of moving particles) and a gas phase with low solids concentration (the *freeboard*) in the reactor.
- The fluidization gas tends to form bubbles with low solid concentrations within the bubbles, which grow in size with bed height.
- The industrial systems can reach quite large cross-sectional reactor areas but are limited in bed height due to bubble formation.
- The possibility of introduction of secondary gases is limited.
- The systems are generally used when very fine particles have to be handled and reaction times are in the range of hours, as in the case of slow diffusion-controlled reactions.
- A standard application is roasting of ZnS ore. OT has built roasters up to $123\,\mathrm{m}^2$ (12.5 m diameter).

2.1.2. The 'expanded' fluidized bed

- Gas velocities are higher as compared with the classical fluidized bed ($u = 2.0$–$5.0\,\mathrm{m/s}$).
- There is no distinct surface in the reactor bed; the whole reactor system is filled with particles but a gradient of particle concentration still exists over the reactor height with high concentrations at the bottom, decreasing exponentially with height.
- The recirculation of particles within the reactor is quite high but horizontal mixing of particles like in a stationary bed is also possible.
- A certain amount of particles will be entrained in the off-gas from the reactor; therefore, a recycling cyclone has to be installed to separate and recycle them back to the reactor.
- The external recycling of particles over the recycle cyclone is limited. Therefore the system cannot be used for high exothermic reactions like combustion chambers where heat has to be removed in the recycle line, such as in a fluidized-bed cooler. The system has advantages for endothermic reactions, solids retention times of 20–60 min and wide particle distribution.
- Secondary gases can be easily introduced and mixed.

2.1.3. The 'circulating' fluidized bed

- High gas velocities ($u = 3.0$–$9.0\,\mathrm{m/s}$) increase particle concentrations also in the upper part of the reactor, but a particle concentration gradient over the reactor height still exists.
- Particles rise in the middle of the reactor and flow back down with high velocities near the reactor walls. This boundary layer of particles with downwards velocity increases from the top to the bottom of the reactor. Horizontal mixing of particles is limited. It mostly occurs in the lower part of the reactor where the down-flowing particles turn direction to rise and go through a 'zero' vertical-velocity component.
- Large amounts of particles get entrained in the off-gas and have to be recycled via recycling cyclones. Heat could be removed to cool the product and/or generate steam, which is advantageous for combustion processes.
- The difference between the gas phase and the particle (the *slip velocity*) reaches a maximum, therefore heat and mass transfer rates are about 10 times greater than for classical fluidized-bed systems.

2.1.4. The flash reactor

- Gas velocity is further increased (10–30 m/s) and this leads to a continuous distribution of particles over the reactor height.
- The direction of particle velocity is upwards only, like in a pneumatic transport-system. Particle mixing (vertical as well as horizontal) practically does not occur.
- The retention time for the particles in the reactor is short, mainly of the same magnitude as the gas-retention time.
- The slip velocity is the lowest of all fluidized-bed systems, adversely affecting heat and mass transfer rates. Flash reactors do not show isothermal behaviour and can only be applied for heat-resistant materials.
- Industrial applications are for cases where the main focus is on transport of material, and/or where short reaction times are acceptable (*e.g.* for heating).

All four categories of fluidized-bed reactor systems have been widely used by OT for various process applications.

2.2. Testing and plant design

Metallurgical processes use natural materials, which vary considerably in chemical and physical characteristics as well as in their fluidization and reaction behaviour. Therefore, testing of materials is a pre-condition to determine their suitability for a particular process and to obtain design parameters for an industrial plant, prior to commencing preliminary engineering for establishing the economic feasibility of the project. The test data is subsequently used for final plant design.

OT generally uses a phased program of testing at its bench-scale and pilot-plant fluidized bed testing facilities at its R&D Centre in Frankfurt. This enables the development of customized processing procedures to optimize the reactor design and the related flowsheet. Support for optimizing the raw material characteristics for maximizing yields is provided by the in-house material beneficiation laboratory.

For this purpose different pilot plants with 200, 350 and 700 mm inner diameters and heights of 6, 10 and 10.5 m, respectively are available. In continuous test operation, effects like agglomeration/sticking, accretion on walls, particle decrepitation and recycle/off-gas dust circuits can be studied as well as off-gas analyses for dust load and chemical composition.

2.3. Scale-up approach for circulating fluidized-bed systems

Over the course of time, considerable knowledge and experience in developing scale-up criteria for plant design has been accumulated. This has accrued from over 50 years of experience in engineering and supply of fluidized bed reactor plants starting from R&D testwork. In the early stages of CFB process development, a mathematical model was developed based on information generated from pilot operations. The model was subsequently continuously updated, refined and tested as a dynamic model from operating data from several CFB industrial plants. These criteria are applied even today in the scale-up of plants.

For the design of new CFB plants, the data and process parameters developed for the new plant, such as particle size, fluidizing gas, gas velocity, etc., are compared with data from existing CFB operating plants in dimensionless units.

To illustrate the scale-up approach, one important tool is the use of the dimensionless particle *Froude* number, defined as follows:

$$Fr_{\mathrm{p}} = u/\{d_{\mathrm{p}}g(\rho_{\mathrm{s}} - \rho_{\mathrm{g}})/\rho_{\mathrm{g}}\}^{1/2} \tag{1}$$

where u is the superficial velocity, m/s; d_{p} the mean particle diameter, m; g the 9.81 m/s^2; ρ_{s} the density of solids, kg/m^3; ρ_{g} the density of gas, kg/m^3.

As ordinate the dimensionless *Archimedes* number is used, defined as

$$Ar = \{(\rho_{\mathrm{s}} - \rho_{\mathrm{g}})\rho_{\mathrm{g}}\}(d_{\mathrm{p}})^3 g/\eta^2 \tag{2}$$

where η is the viscosity of gas, kg/(m/s).

The different particle *Froude* numbers demonstrate the different objectives of the process applications. A comparison of the Fr_{p} numbers calculated for the projected plant based on design parameters obtained from testwork with existing numbers from plants previously built and in operation is made.

Table 2
Classification of fluidized-bed systems using particle *Froude* number

System	Fr_p	Applications
Classical fluidized bed (Bubbling Bed)	0.05–0.35	Zn/Cu/Au-sulfide roasting; Final reduction of iron ore
Expanded fluidized bed	1.0–1.5	Pre-reduction of iron ores Gold-ore roasting,
Circulating fluidized bed	2.0–2.5	Coal combustion, Calcination of alumina;
Flash heater	4.0–4.5	Pre-heating of ilmenite

From this a confirmation for one of the important design parameters is obtained. According to the above-defined reactor categories, the Fr_p numbers listed in Table 2 can be classified.

3. SOME ADVANCED METALLURGICAL AND MINERAL APPLICATIONS

3.1. Non-Gold roasting applications

Some examples of fluidized bed plant systems form some non-gold applications are given here to illustrate cases where very specific process requirements have to be fulfilled; some of these may have a bearing in gold-ore applications.

3.1.1. Alumina calcination

In the alumina-calcining sector, OT has built to date 46 CFB plants with a total annual installed capacity of approximately 22 million tons of alumina, thus representing a world market share of approximately one-third.

The purpose of the calcination plant is to produce metal-grade alumina from aluminium *tri*hydrate. The filtered hydrate is dried, dehydrated and calcined to the required alumina quality. After pre-heating and partial dehydration, the final calcination takes place in the calcination stage, which consists of the fluid-bed furnace, recycling cyclone and seal pot. The required heat for calcination in the fluid bed furnace is generated by direct combustion of fuel in the fluid bed. The fuel, which is to undergo combustion, is fed into the fluid bed through fuel lances, which are arranged above the nozzle grate of the furnace.

Due to the intensive mixing and heat exchange that takes place in the fluidized bed, the furnace temperature adjusts itself as a mixed temperature between the combustion temperature and the solids temperature, and is kept steady at a pre-set level. In the lower furnace zone, between the grate and the secondary air inlet, a fluid bed of high solids concentration is adjusted. In the upper furnace zone, the internal recirculation of the solids causes a continuous reduction of solids concentration until a relatively low concentration is reached. With this solids concentration, the hot gases enter the recycling cyclone where they are separated from the solids. The hot alumina, which is separated in the recycling cyclone passes through the seal pot and re-enters the fluid bed furnace. The recirculation of the solids leads to uniform and practically identical solids and gas temperatures in the entire calcination stage. The alumina, which is discharged from the calcining stage, is cooled in two cooling stages each of which consists of a lift-duct and a secondary air cyclone. The third cooling stage is designed as a fluid-bed cooler.

3.1.2. Pre-heating, pre-reduction and direct reduction (DR) of iron-ore fines

The direct reduction of iron-ore fines without an intermediate agglomeration stage has been an interesting challenge for process developers in the past. The constraining factor has been the so-called *sticking* tendency of reduced or metallized fines, which is particularly prevalent and difficult to control in the case of gas-based direct reduction. With most of the available iron ores, this phenomenon tends to appear already at a fairly low-temperature threshold of $\geqslant 650\,^{\circ}\mathrm{C}$. For OT's gas-based *Circored*® DR process, which has been industrially proven at a 500,000 t/y HBI (hot briquetted iron) plant in Trinidad, hydrogen was selected as a single reducing agent. The main reasons for this choice were its superior low-temperature ($\sim 600\,^{\circ}\mathrm{C}$) reduction reaction characteristics, the low conduciveness of the reduced material to sticking and avoid the low-temperature, high-pressure methanation tendency if CO were present. The principle of the *Circored*® pre-heater is applied for pre-heating and partial reduction of the iron ore fines for the *HIsmelt*® smelt-reduction plant at Kwinana, Western Australia, for a capacity of 800,000 t/y of hot metal.

The *Circofer*® process uses fundamentally the same two-stage CFB/FB configuration for the core plant for obtaining highly metallized product as in the case of *Circored*®. The precursor of the coal-based *Circofer*® process of OT was the pre-reduction CFB reactor for the *Elred* smelting reduction pilot plant in Sweden, which operated for 3 years in the late 1970s. A heater for coal charring and circulatory material heating has been integrated into the CFB circuit for which oxygen is injected into the heater. The process operates at 4 atm at a temperature of approximately 900 °C.

3.1.3. Charring of high volatile-matter (VM)-containing coals with pre-reduction

As a spin-off of the development of coal-based direct reduction in the CFB reactor, a natural outcome has been to use it for the combined charring of high volatile coals with pre-reduction of iron-ore fines (*Circochar*® process) as a primary stage for smelting/reduction processes. Alternatively, charring of high volatile partially pre-dried coals alone can be performed in the CFB reactor for use in metallurgical processes. The moderately rich H_2/CO-containing off gas at approximately 900 °C can be used for reduction processes or for raising steam for power generation. Large-scale pilot plant tests have confirmed the viability of the process concepts, which are now available for industrial application.

3.1.4. Oxidation and pre-treatment of Ilmenite

For the production of synthetic rutile (~95% TiO_2) using the Becher Process, in the first step it is necessary to oxidize the ferrous iron in the ilmenite mineral to the ferric state prior to the iron-reduction stage, where metallic iron is formed. In a new development, CFB and flash reactors are envisaged for the primary oxidizing and reduction stages as well as for product calcining for the first time. This not only allows the use of lower-grade feed materials but also enables a considerable increase in capacity as compared to the conventional processing routes and a substantial improvement in product purity. The reaction conditions have to be controlled very closely to obtain an optimum product, a requirement that can be easily met by CFB and flash systems being provided.

3.1.5. Oxidation and reduction of laterite Nickel ores

OT has developed a process for the oxidation and reduction of laterite nickel ores where the reduction of iron and nickel to the wuestite/metallic states respectively, is performed in a fluidized bed reactor using reduction gas generated very cost-effectively from natural gas in an autothermal catalytic reactor. The process of reduction and calcination is energy optimized. It uses the off-gas from the fluidized bed reduction reactor and still contains sufficient amount of energy to dry and calcine the nickel-ore fines in a primary-stage CFB reactor. The product is obtained with a high content of metallic nickel (> 90% of total nickel) and iron in the wuestite state. This results in considerable energy savings in smelting with the pre-reduced product.

3.2. Roasting of refractory gold - ores

Refractory gold-ores are characterized by low gold recoveries in direct cyanide leaching. Gold particles are either embedded in sulfide components or absorbed on carbon surfaces during the leaching process. Oxidizing roasting of such ores prior to leaching is an effective step to increase gold recovery typically to levels above 90%. To achieve good gold recoveries in the subsequent leaching steps, the majority of the sulfur and carbon has to be oxidized to SO_2 and CO_2. If arsenic is present, it has to be transformed to the volatile trivalent compound. The stable pentavalent compound is formed under uncontrolled oxidation conditions and ends up in the calcine and finally in the leaching stage. The volatile trivalent compound reports to the waste gas and can be separated during waste gas cleaning. In such cases arsenic is reduced to relatively low levels in the calcine.

For optimum gold recovery the roaster must work within a narrow operation window regarding temperature and oxygen partial-pressure. The inherent stability of temperature and gas composition within the entire CFB furnace system provides roasters of this type with significant advantages in this application. Different ores require different temperature levels. These temperature levels are usually in the range 550–720 °C. The individual roaster is then operated within $\pm 10\,^{\circ}C$ of its set point. Despite the modest temperature levels, the following criteria are reliably met:

- High sulfur removal and carbon combustion.
- High arsenic removal, if applicable.
- Safe and controlled combustion of support fuels such as coal, kerosene and diesel.
- High specific throughput per roaster unit.
- Excellent process control due to typical circulating fluidized-bed characteristics.
- Removal of sulfur by *in situ* capture or by production of sulfuric acid.

The sulfur of the ore and fuel can be removed by producing sulfuric acid (as at the Newmont plant) or by using the *in situ* capture with lime or dolomite. The alternative that is selected depends on SO_2 concentration, demand for sulfuric acid and environmental regulations.

The *in situ* capture of SO_2 arising from the combustion of sulfur-bearing fuels or ores by a sorbent or reagent involves the following reactions:

$$\text{Decomposition}: \ CaCO_3(s) \rightleftharpoons CaO\,(s) + CO_2(g) \tag{3}$$

$$\text{Sulfurization}: \ CaO(s) + SO_2(g) + \tfrac{1}{2}O_2(g) \rightleftharpoons CaSO_4(s) \tag{4}$$

$CaCO_3$ is normally present in the form of limestone or dolomite in sulfidic ore roasting. The reactions of $MgCO_3$ are identical. *In situ* SO_2 capture involves various chemical and physical mechanisms, which take place either simultaneous or successively. These are:

- Oxidation of sulfur to SO_2.
- Calcining of $CaCO_3$ to CaO resulting in an improved microstructure, *i.e.*, large surface area of the sorbent or reagent.

- SO_2 and O_2 transport to CaO grain boundaries.
- $CaSO_4$ formation in the form of a $CaSO_4$ layer on the CaO grain boundaries.
- Size reduction of the sorbent particles through abrasive action in the circulating fluidized bed and repeated particle recirculation via the recycling cyclone, resulting in the repeated formation of new CaO boundaries.

The attainable Ca conversion rates are limited by the mass transport mechanism of the individual particle and retention times of the sorbent particles in the system. A low SO_2 emission level (*i.e.*, sulfur capture as high as 98%) can be achieved by adding above-stoichiometric amounts (Ca:S >2) of sorbent.

The amount of sorbent that is required to achieve a specified SO_2 emission level is influenced by the following factors:

- Process conditions (*e.g.*, temperature, particle retention time).
- Sorbent properties (*e.g.*, Ca and Mg content, reactivity).
- Fuel properties (*e.g.*, sulfur content and distribution, Ca and Mg content).

The degree of SO_2 capture in the CFB shows a high degree of temperature dependence. The sorbent demand increases if the combustion temperature is outside the optimum range of about 800–850 °C. The temperature effect can be attributed to insufficient calcination at lower temperature, and possibly, to a faster pore-mouth closure that limits SO_2 diffusion to the inner sorbent surface at higher temperatures. Therefore, the roasting temperature has to be controlled in a very narrow window of ± 10°C, a requirement that

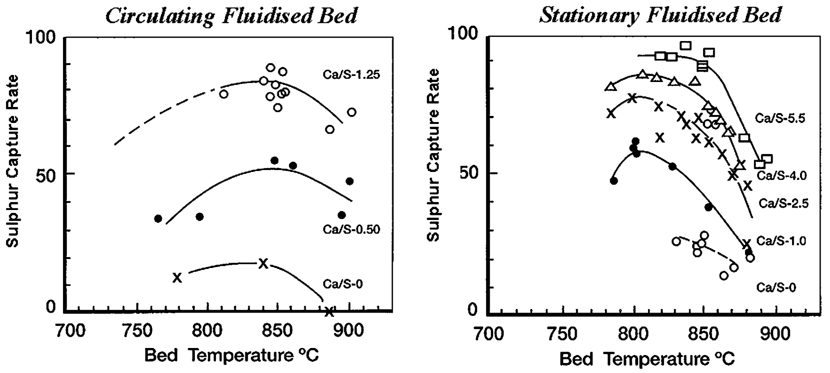

Fig. 1. Capture rate of sulfur transferred from gas phase by reacting to $CaSO_4$, depending on Ca:S and temperature in circulating and stationary FB systems.

can be fulfilled excellently by CFB systems. Fig. 1 shows the temperature and Ca/S-dependence of sulfur capture in the Stationary Fluidized Bed and the Circulating Fluidized Bed:

The circulating fluid-bed achieves high sulfur capture rates over a wide temperature range. At a moderate Ca:S ratio of around 1, a sulfur capture rate significantly above 50% is achieved. This reduces the requirement for limestone (or dolomite) and uses the *in situ* material that is available much more efficiently.

Besides the temperature and stoichiometric ratio of Ca:S, the particle-size distribution in the CFB has influence of a significant effect on the SO_2-conversion rate. This effect can be explained by the particle-retention time on Ca conversion. Both the particle-retention time and the particle-size distribution pertaining to in the solids inventory under steady-state conditions are determined by the interactions of the following factors:

- Particle-size distribution of the fuel (coal or oil).
- Degradation behaviour of material and sorbent
- Collection efficiency of recycling cyclones.

Here the CFB and FBB systems are largely identical in behaviour. The separation effect of the fluidized-bed/cyclone system leads to shorter retention time for small particles sizes, which affects good Ca conversion. Apart from the particle size of the feed, the abrasion behaviour of the sorbent has a significant influence on the particle size in the system.

4. PERFORMANCE OF EXISTING CFB GOLD ROASTERS

Several circulating fluidized-bed reactors with throughputs up to 3,000 t/d have been built with excellent results in gold recovery. Examples for gold-ore roasting operations are given below.

4.1. Kalgoorlie Consolidated Gold mines – Gidji, Western Australia

The first commercial application of CFB roasting technology for treatment of sulfidic gold-concentrates was at the Gidji plant in Kalgoorlie, Western Australia. Following initial roasting tests with concentrate, this plant was commissioned in June 1989. The facility was designed and constructed within 15 months of contract award. Before the first plant was operational, a second CFB roasting plant, of similar design and capacity was also ordered for the facility. Hot commissioning of this second plant was successfully completed in July 1990. Today both plants achieve excellent gold recoveries. Table 3

Table 3
Operating and performance data for Gidji roasting plant

Parameter	Value
Roaster feed (t/d)	360–640
Average roasting temperature (°C)	640
Excess roasting air (%)	>5
Average solids residence time (min)	30
Range of concentrates sizes (% –38 μm)	~55
Gold leach recovery (%)	~95

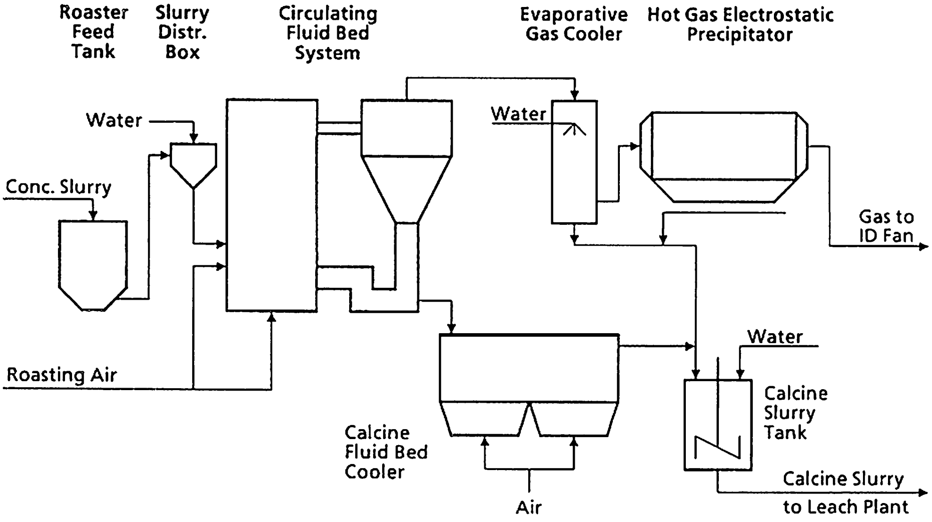

Fig. 2. CFB roasting plant at Gidji.

shows the typical operating and performance data for the roasting plant, feeding 33.3% sulfide sulfur in form of pyrite:

The plant consists of the CFB roaster with its slurry-feed system, followed by on evaporative gas-cooler, hot-gas electrostatic precipitator and induced-draft fan. The calcined product discharged from the CFB system is cooled with air in a fluid-bed cooler and then quenched together with the precipitator and gas-cooler dust in a slurry tank (see Fig. 2).

4.1.1. Slurry-feed system

The concentrate slurry is fed by centrifugal slurry-feed pumps into the distribution box located in the structure near the upper part of the reactor.

The function of the slurry distribution is to equally apportion the incoming slurry to four *tundishes*, which in turn each feed by gravity into a roaster feed gun. The reactor is therefore fed by four slurry-feed guns. The slurry-feed guns are installed around the circumference of the conical part of the roaster. Plant air is supplied to the feed guns to spray the slurry feed into the bottom part of the fluid bed.

This simple circuit is very reliable and provides an even distribution to the furnace, consistent feed quality and the ability to add water to the feed system for roasting temperature control. This gravity feed system has been operating well with feed slurry containing up to 70% solids w/w.

4.1.2. Roasting

During operation, the sulfur:air ratio and the reactor-temperature profile in the roaster can be precisely controlled. A further process parameter is the differential pressure between furnace bottom and furnace top. This is an indicator for the retention time, at a given feed rate. The roaster reactions are complete by the time the entrained solids are carried through the recycle cyclone. This entrainment results in a recirculation of several hundred tonnes per hour of calcine through the roaster/recycle cyclone loop. This substantial recirculation provides the thermal inertia, which contributes to the excellent process stability and uniformity of calcine quality. With this degree of control, under- and over-roasting can be virtually eliminated. This in turn results in maximum gold recovery without the formation of excessive sulfate.

4.2. Placer Dome – Cortez, Nevada

The first Lurgi CFB roaster for whole-ore roasting was installed at Cortez Gold Mines in Nevada and commissioned in 1990. It was designed for calcining 1960 t/d of gold-bearing refractory ore. The measured SO_2 concentration in the off-gas was about 100 vppm. Therefore there was no need for installation of an SO_2 treatment plant.

4.2.1. Roasting

The CFB consists of a reactor, cyclone, seal pot, fluidizing air-blower, oxygen pre-heater, an induct burner for heating fluidizing gas, and a calcine cooler for cooling the roasted product. The ore contains on average 1.1% sulfide sulfur, 1.1% organic carbon and 2.9% carbonate carbon. The relatively high carbon content affects the gold recovery through *preg-robbing* during leaching. After roasting in the CFB, the carbon content is reduced to such low levels that the gold recovery increases by approximately 20%. The limestone introduced to the process with the ore reacts with SO_2, forming gypsum at a reactor temperature between 680 °C and 720 °C (refer to Eqs. (3) and (4)).

The ore flows by gravity through an inclined chute from the ore bin into the roaster. The discharge of the partially oxidized ore takes place at the seal pot. The discharged calcine is cooled down in the calcine cooler, where further oxidation takes place. The hot calcine is cooled by direct and indirect heat-exchange. Liquid sulfur and kerosene can be injected into the roaster as required to maintain the heat balance. The air for the roaster flows countercurrent to the calcine flow. The pre-heated air from the calcine cooler is injected into the roaster. The fluidizing tail gas leaves the calcine cooler and passes through a filter to separate the entrained dust before entering the roaster as secondary air. The calcine product is quenched and the warm slurry undergoes neutralization with milk of lime, thickening and conventional carbon-in-leach processing. Thickener overflow passes through cooling sprays and a final cooling pond for recycle.

4.2.2. Gas cleaning operation

The cooled gas passes through a scrubber and a hot electrostatic precipitator, where most of the remaining dust in the gas steam is removed. The collected dust is removed from the electrostatic precipitator by two chain conveyors located at the bottom of the unit, as shown in Fig. 3.

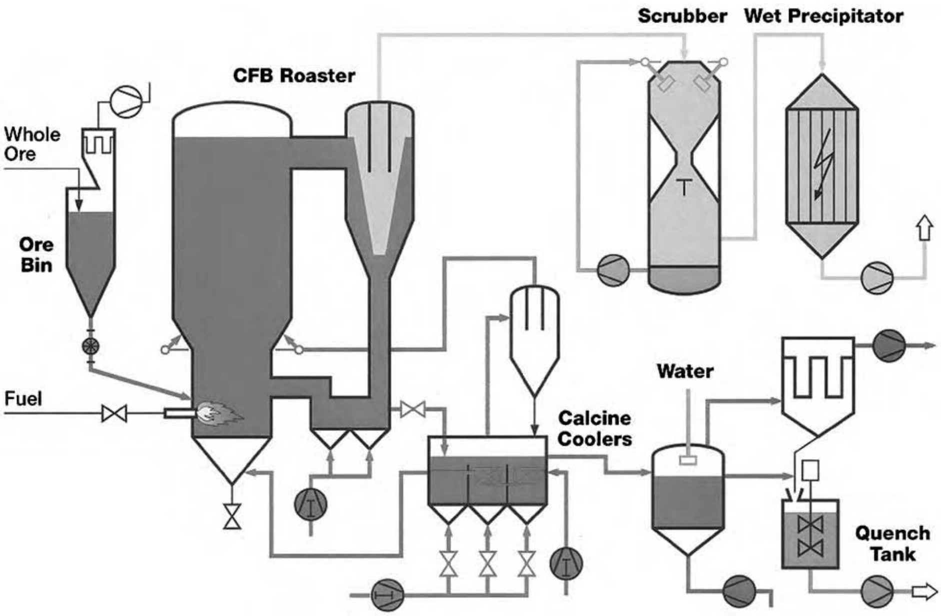

Fig. 3. Cortez CFB roasting plant.

Table 4
Operating and performance data for Newmont Nevada roasting plant

Parameter	Value
Roaster feed (t/d)	7800
Oxygen consumption (t/d)	610
Natural gas consumption (Nm^3/t)	17.5
Power consumption (kWh/t)	7.36
Sulfuric acid production (max) (t/d)	410
Gold head grade (g/t) oz/t	8.8
Gold recovery (%)	90.5

4.3. Newmont Gold Company – Nevada

The plant was constructed in 1993 and consists of two lines. The main process steps of the Newmont plant in Nevada, USA are:

- Ore pre-heating operation.
- Roasting operation.
- Gas cleaning operation.
- Sulfuric acid plant.

Table 4 illustrates the average production data and consumables at design throughput.

The processed gold ore consists mainly of quartz (70%), with 1.5–2.5% sulfur and approximately 0.4% organic carbon.

4.3.1. Ore pre-heating operation

After crushing, screening and grinding of refractory gold from different deposits and reserve stockpiles, the finely ground refractory ore is delivered by a pneumatic air-slide conveying system to two roaster day bins (one per roaster train). Ore is withdrawn from the day bin by two dosing valves and the feed chute into the ore pre-heater.

The pre-heater system includes the following major pieces of equipment: CFB ore pre-heater with two cyclones and two seal pots; induced-draft fan and two primary air blowers. The ore is pre-heated to 215 °C by primary air, which enters the bottom of the CFB pre-heater at a design temperature of 435 °C after been heated in two stages. In the first stage, ambient air provided by two primary air blowers is heated to 200 °C by indirect heat transfer from the hot calcine. The partially heated primary air is heated to the desired temperature by burning with natural gas in an inductor burner just ahead of the pre-heater.

The CFB ore pre-heater drives off the remaining free moisture in the ore ($<1\%$) with an average retention time in the range of 2–5 min. Two cyclones and two seal pots are installed for solid recirculation. A portion of the material recycles into the pre-heater, and the balance is discharged through a discharge lance to flow by gravity down a chute to a roaster. Entrained solids in the gas leaving the cyclones are captured in a single baghouse and discharged into the roaster. The pre-heater operating temperature is limited to 420 °C because higher temperatures may result in partial oxidation of sulfide minerals with SO_2 evolution and mercury volatilization. Exhaust gases from the baghouse from both ore pre-heaters are combined before entering a caustic scrubber to control SO_2 emissions. A portion of the de-dusted exhaust gases (at ~200 °C) can bypass the caustic scrubber and be recycled to the grinding circuit in order to reduce the natural gas consumption in the drying process.

4.3.2. Roasting operation

Each roaster train is an integrated system consisting of a CFB reactor, which includes two cyclones and two seal pots, fluidizing air-blower, oxygen pre-heater, an induct burner for heating fluidizing gas and two calcine coolers for cooling the roasted product. During an average retention time of up to 10 min and a roaster temperature of ~550 °C, the sulfide minerals and the organic carbonaceous compounds are oxidized.

Pre-heated ore flows by gravity through an inclined chute, which connects the pre-heater and the roaster. The partially oxidized ore is discharged through the seal pot discharge lances into the calcine coolers where further oxidation takes place. Liquid sulfur is injected into the roaster as required to maintain the heat balance and the SO_2 concentration in the sulfuric acid plant. The hot calcine is cooled by direct and indirect heat exchange. Acid plant tail gas is used as fluidizing gas in all four chambers of the cooler. Oxygen enrichment can be supplied to Chambers 1 and 2 to enhance further oxidation. The fluidizing tail gas leaves the calcine cooler and passes through a cyclone to separate the entrained dust before entering the roaster as secondary air.

The calcine product (roaster ore) is quenched at 15% solids and the warm slurry (at 40 °C) undergoes neutralization with milk of lime, thickening and conventional carbon-in-leach processing. Thickener overflow passes through cooling sprays and a final cooling pond for recycle. The roaster off-gas is cooled in a waste heat boiler from 550 °C to 375 °C. Superheated steam is generated in the gas-cooling process for use in the SO_2 fan turbine. The cooled gas passes through a hot electrostatic precipitator where most of the dust in the gas steam is removed. These units are designed to handle a combined flow of 1700 m^3/min of flue gas with high a dust loading. The collected dust is removed from the electrostatic precipitator by two chain conveyors located at the bottom of the unit (see Fig. 4).

A portion of the de-dusted flue gas (typically about 50%) is taken just after the hot electrostatic precipitator and recycled to the roaster, with the balance

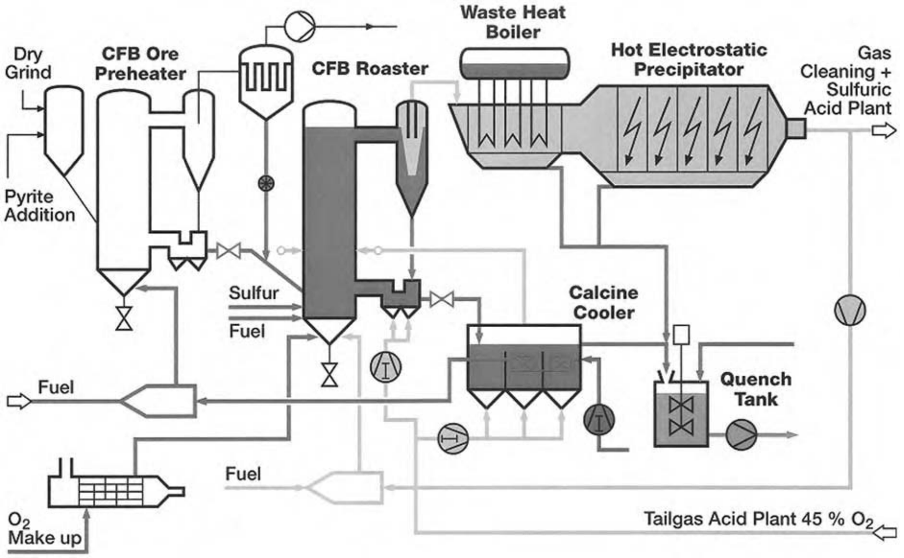

Fig. 4. Newmont CFB roasting plant.

going to the gas cleaning and acid plants. The recycled gas to the roaster, which contains 30–40% oxygen, is reheated with natural gas in an induct burner and blended with pre-heated pure oxygen to maintain the desired oxygen concentration in the roaster.

4.3.3. Gas-cleaning operation

The primary unit operations in the gas-cleaning plant are gas washing, moisture removal by cooling, sulfuric-acid mist removal by wet-gas electrostatic precipitators, fluorine removal, mercury removal and recovery of mercury by electrowinning. The portions of the gas stream that is not recycled to the roaster are combined and enter the gas washing and cooling section of the plant, which consists of a wash tower and two gas coolers. The hot gas (380 °C) enters at the bottom of the wash tower and flows counter-current to the scrubbing solution. The evaporation process cools the gas to the exit temperature of 70 °C, saturates the gas stream with moisture, absorbs some SO_3 in the gas and condenses volatile impurities from the gas stream. Cooling of the gas to final temperature of 30 °C is accomplished by two two-stage gas coolers, which are essentially tube-and-shell heat exchangers. After the gas exits the coolers, it enters the first of two identical wet electrostatic precipitators to remove acid mist and the small amount of very fine dust from the gas stream. Poor performance of the SO_3 mist eliminators will result in low efficiency of the mercury-removal plant and high mercury levels in the product acid.

Fluorine in the roaster off-gas is removed since it will react with the acid-plant catalyst, thus reducing its service life. The fluorine-removal tower is located between the two wet-gas electrostatic precipitators. The gas enters the tower at the top and passes down through a bed of high-silica packing where 80% of the fluorine is removed by chemical reaction with the silica packing.

Mercury compounds in the refractory ore feed are volatilized during the roasting process and report in the gas stream. Some of the mercury reacts with other compounds or condenses during the washing and cooling process. However, a significant amount of metallic mercury remains in the gas stream and, if not removed, will contaminate the sulfuric acid product. The mercury removal plant consists of a mercury tower, where metallic mercury in the gas reacts with the mercuric chloride in the scrubbing solution to form mercurous chloride (calomel); the mercuric chloride solution enters the electrowinning cells for metallic mercury recovery.

4.3.4. Sulfuric acid plant

The sulfuric acid plant can be divided into three main sections: drying and adsorption, SO_2 converter with gas-to-gas heat exchangers and tail gas scrubber. The plant uses the 3 + 1 double absorption system. The acid plant can operate in four production modes. Modes 1 and 3 are for production of 94% sulfuric acid and Modes 2 and 4 for 98.5% sulfuric acid production. Any mode of operation can use single, double or partial-double absorption depending upon the incoming SO_2 concentration in the process gas. The final SO_2 conversion is typically greater than 99.8%.

4.4. Newmont Gold Company – Minahasa, Indonesia

OT's latest CFB application is the Minahasa roaster, which has a capacity of 2,160 t/d. It commenced operation in early 1997 and achieved its plant guarantees within 3 weeks of start-up. In commercial operation, it has achieved gold recovery of over 93%. The plant consists of:

- The circulating fluid-bed reactor with cyclone and seal pot.
- An evaporation cooler, which conditions the gas to the electrostatic precipitator by reducing its temperature.
- A hot electrostatic precipitator.
- A calcine cooler.

4.4.1. Roasting operation

The plant was designed to roast refractory ore at a rate of 90 t/h within a very narrow temperature range, less than ±7.5 °C, at an operating temperature of 580 °C. The precise operation within the reaction window is important in order to achieve maximum gold recovery. The gold recovery rate drops by several percent when this temperature window is exceeded. Lower temperatures cause insufficient burn-out of the preg-robbing carbon. Sulfide sulfur and organic carbon contents in the roaster material were reduced from 1.37% S to <0.01%, and organic carbon to 0.02%.

The roaster area is approximately 8 m^2. Kerosene and coal were tested successfully as auxiliary fuels to supply the energy demand of ores with low heating values. Calcine cycles between roaster-cyclone and seal pot. The discharge of the calcine takes place in the seal pot and flows to the calcine cooler. The hot calcine is cooled by direct and indirect heat-exchange in the calcine cooler. The fluidizing tail gas leaves the calcine cooler and passes through a cyclone to separate the entrained dust before entering the roaster as secondary air. The calcine product (roaster ore) is quenched and the warm slurry (at 60 °C) is pumped to the leaching plant.

The roaster off-gas is cooled in evaporation cooler from 580 °C to 375 °C. The off-gas volume flow increases from approximately 35,300 to 44,000 Nm^3/h. The cooled gas passes through the hot electrostatic precipitator where most of the dust in the gas steam is removed. Three chain conveyors located at the bottom of the unit remove the precipitated dust from the evaporation cooler and the electrostatic precipitator. The dust is transported to the hydrocyclone and leaves together with the calcine coming from the calcine cooler over the quench tank in the roasting plant (see Fig. 5).

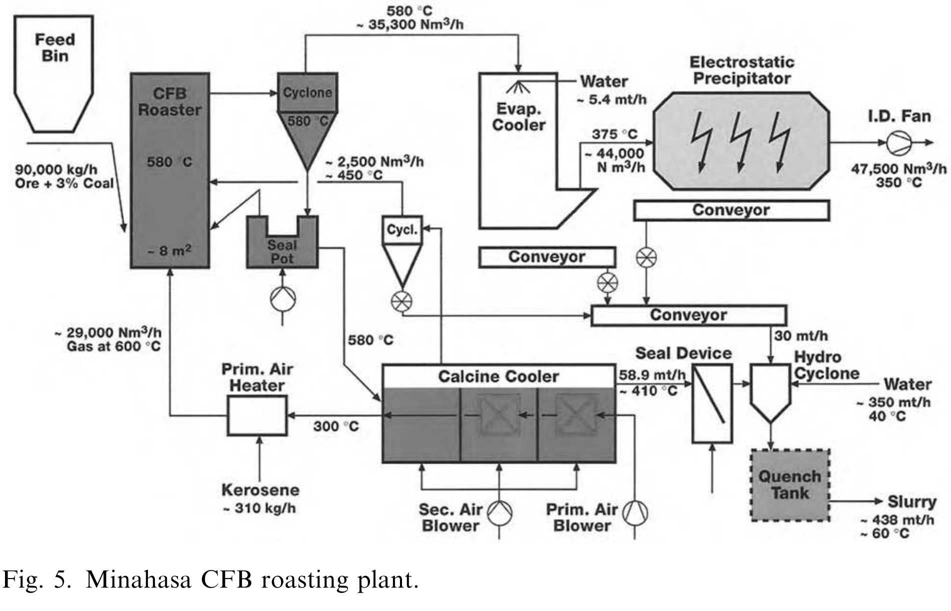

Fig. 5. Minahasa CFB roasting plant.

5. CONCLUSIONS

During the past 15 years, CFB technology has been successfully applied to the roasting of refractory gold ores and concentrates on both pilot plants (200, 350 and 700 mm furnace inner diameters) and commercial CFB roasting plants. The CFB provides conditions for enhanced heat and mass transfer, supporting nearly "ideal" isothermal conditions and fast reaction kinetics. Outokumpu Technology (former Lurgi Metallurgie) has to date installed more than 70 CFB applications for different materials. Considerable knowledge and experience in developing scale-up criteria for plant design has accrued from over 50 years of experience in engineering and supply of fluidized bed reactor plants.

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II.4 *Leaching*

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Chapter 19

Heap leaching of gold and silver ores[☆]

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Heap leaching of gold and silver ores is conducted at approximately 120 mines worldwide. Heap leaching is one of several alternative process methods for treating precious-metal ores, and is selected primarily to take advantage of its low capital cost relative to other methods. Based on surveys of about 60% of the known heap-leach operations, it is likely that heap leaching produces 12% of the world's gold. In 2004, at least 10 major heap leaches were in the late design stages, in such diverse locations as Brazil, Kazakhstan, Laos, Mexico, Peru, the United States and Uzbekistan. Heap leaching for silver is conducted using the same principles and operating practices as for gold, but heap-leach operations produce only a small fraction of world silver production.

1. INTRODUCTION

Heap leaching had already become a fairly sophisticated practice at least 500 years ago. Georgius Agricola, in his book *De Re Metallica* (published in 1557), illustrates a heap leach with a 40-day leach cycle (Fig. 1), which could pass in many ways for a modern heap leach. The Agricola heap-leach recovered aluminum (actually alum) for use in the cloth-dying industry. Copper heap and dump leaches in southern Spain were common by about 1700.

[☆] An expanded version of this paper, including survey results of industry practice in many operating areas, can be found in the book *Mineral Processing Plant Design, Practice and Control*, SME, 2002 (www.smenet.org).

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Fig. 1. "The rocks are . . piled in . . heaps fifty feet long, eight feet wide and four feet high, which are sprinkled for forty days with water. The rocks begin to fall to pieces like slaked lime, and there originates a . . new material". (Drawing and text from *De Re Metallica*; Agricola, 1556).

Gold and silver heap-leaching began with the first Cortez heap leach in 1969. While many projects have come and gone, Cortez is still going – their new 63,000 t/d South Area leach started up in 2002.

The largest U.S. precious-metal heap-leach is the Round Mountain operation in Nevada, with over 150,000 t/d of ore going to crushed or run-of-mine heaps, at an average grade of 0.55 g/t (this chapter follows the convention of *ton* for short ton and *tonne* for metric ton; t/d reflects metric tonnes). Worldwide, Newmont's Yanacocha operation in Peru holds the record, with a production rate of 370,000 t/d, at an average total reserve gold grade of 0.87 g/t. On the other end of the scale, some very high-grade ores – up to 15 g/t (0.5 oz/ton) – are being successfully processed at rates of several hundred tonnes per day (Sterling, Nevada; Hassai, Sudan; Ity, Ivory Coast).

Nevada was the 'birthplace' of modern gold heap-leaching in the late 1960s, and is only now giving up its dominance of this technology. Other very large gold districts – notably the pre-Cambrian shield areas of Canada, Australia and South Africa – show relatively few heap leaches. There are several reasons for this geographic concentration, but the primary reason is that Nevada gold deposits tend to have been created by low-energy geologic processes – near-surface hot springs and moderate depth, hydrothermal systems that deposited low-grade gold in permeable rocks. Besides aiding gold deposition, the permeable nature of the rocks allowed uniform and deep oxidation that liberated the gold from its sulfide and carbonaceous host minerals. In contrast, Shield deposits have generally had a more complicated history, which has resulted in coarse gold contained in poorly permeable rocks. Often these ores can be successfully heap leached only after weathering has completely destroyed the rock matrix.

1.1. What is heap leaching?

To those of us in the gold industry, the question "What is Heap Leaching?" seems to have an obvious answer. In the simplistic sense, heap leaching involves stacking of metal-bearing ore into a *heap* on an impermeable pad, irrigating the ore for an extended period of time (weeks, months or years) with a chemical solution to dissolve the sought-after metals, and collecting the leachant (*pregnant solution*) as it percolates out from the base of the heap. Fig. 2 is an aerial photograph showing the typical elements of a precious-metals heap-leach operation – an open-pit mine, a heap of crushed ore stacked on a plastic pad, ponds, a solution process facility for recovering gold and silver from the pregnant solution, and an office facility. For a small operation such as the one illustrated here, very limited infrastructure is required.

In a more complex sense, *heap leaching* should be considered as a form of milling. It requires a non-trivial expenditure of capital, and a selection of operating methods that trade off cost versus marginal recovery. Success is measured by the degree to which target levels and rates of recovery are achieved. This distinguishes heap leaching from dump leaching. In *dump leaching*, ores are stacked and leached in the most economical way possible, and success is achieved with any level of net positive cash flow.

The bibliography of precious metals heap-leaching is quite extensive, but a limited bibliography has been compiled at the end of this chapter.

1.2. Why select heap leaching as the processing method?

Gold and silver can be recovered from their ores by a variety of methods, including gravity concentration, flotation and agitated tank leaching. Methods similar to heap leaching can be employed: dump leaching and vat leaching (*vat leaching* is the treatment of sand or crushed ore in bedded vats with rapid solution percolation). Typically, heap leaching is chosen for basic financial reasons – for a given situation, it represents the best, or safest, return on investment. Some of the financial considerations that might result in the selection of heap leaching are presented below.

Fig. 2. Heap leach installation at Mineral Ridge, Nevada (Golden Phoenix Minerals, Inc.). The open pit mine is shown on the left. On the right is a 2 Mt heap of crushed, conveyor-stacked ore placed on a plastic-lined leach pad. Pregnant and barren solution storage ponds are located downslope from the heap. Buildings include process plant, laboratory, maintenance shop and administration offices. (Photograph courtesy of Tom Nimsic, American Au/Ag Associates).

1.2.1. Capital risk

A heap leach can be installed faster than an agitated-leach plant, and at about one-third the capital cost. This can be a deciding factor when working in politically unstable countries.

1.2.2. Capital is very difficult or expensive to raise

Heap leaching has often provided the route for a small company to grow into a large company.

1.2.3. Lack of sufficient reserves

The Sterling Mine in Beatty, Nevada (Cathedral Gold Corporation) began life as an underground mine, with a reserve of 100,000 tons of ore at a gold grade of 11 g/t (0.35 oz/ton). Over a 15-year period, it mined and processed nearly 1 million tons, but never had enough ore reserves to justify a conventional mill. Fortunately, the Sterling ore achieves excellent heap-leach recovery – the original heaps reached 90% gold recovery from ore crushed to 100 mm.

1.2.4. Equal or better percent recovery

Some ores show the same overall per cent recovery in a heap leach or a mill. At the joint AIME/AusIMM Symposium *World Gold '91*, T. Peter Philip of Newmont presented a paper *To Mill or to Leach?*, in which he evaluated the decision of Newmont to build the Carlin No. 3 mill. He concluded that the mill recovery was over-estimated and the heap-leach recovery underestimated, and that the decision to go with milling may have been incorrect.

1.2.5. Differential recovery is not sufficient to justify added investment

A recent review (Kappes, 1998) concluded that for a 'typical' Nevada-type gold orebody with ore grade of 3.0 g/t (0.088 oz/ton), the mill recovery would have to be 21% higher than the heap-leach recovery to achieve the same return on investment – and this is very seldom the case.

1.3. Chemistry of gold and silver heap leaching

The chemistry of leaching gold and silver from their ores is essentially the same for both metals, and many ores contain a mixture of the two. A dilute alkaline solution of sodium cyanide dissolves these metals without dissolving many other ore components (copper, zinc, mercury and iron are the most common soluble impurities). Solution is maintained at an alkaline pH of 9.5 to 11. Below a pH value of 9.5, cyanide consumption is typically high. Above a pH value of 11, metal recovery decreases.

Silver is usually not as reactive as gold with cyanide. This is because gold almost always occurs as the metal, whereas silver may be present in the ore in many different chemical forms, some of which are not cyanide-soluble. Gold recovery efficiency from operating heap leaches is typically ~70%, although it can range from 50 to 90%. Silver recovery efficiency is typically ~55%.

Other leaching agents, such as thiosulfate, thiourea, hypochlorite and bromine, have been experimented with an alternative to cyanide, but cyanide is by far the most effective and the most environmentally friendly leaching agent. A good discussion of the process chemistry of alternative leaching systems can be found in Chapters 21 and 22.

2. FACTORS INFLUENCING HEAP-LEACH EFFICIENCY

2.1. Type of ore

Heap-leach recovery is very dependent on the type of ore being processed (see also Chapter 2). Some typical examples are discussed below.

2.1.1. *Carlin-type sedimentary ores*

These ores consist of shales and 'dirty' limestones, containing very fine (submicroscopic) gold. Oxidized ores are typically coarse-crushed (75 mm) but may show recovery of 70% or better at run-of-mine sizes. The largest of the northern Nevada heap leaches (Carlin, Goldstrike, Twin Creeks) treat this type of ore. Unoxidized ore contains gold locked in sulfides, and also contains organic (carbonaceous) components, which absorb the gold from solution. Because of the presence of both oxidized and unoxidized ores, the northern Nevada operations (for instance, Barrick's Goldstrike Mine) may employ roasters, autoclaves, agitated-leach plants and heap leaches at the same minesite.

2.1.2. *Low-sulfide acid volcanics or intrusives*

Typical operations treating this type of ore are Round Mountain, Nevada, and Yanacocha, Peru. Original sulfide content is typically 2–3% pyrite, and the gold is often enclosed in the pyrite. Oxidized ores yield 65 to 85% recovery but may have to be crushed to below 12 mm (1/2 in.), although some ores are successfully leached at run-of-mine sizes. At Round Mountain, Nevada, approximately 150,000 tons per day of low-grade oxide ore are treated in truck-stacked run-of-mine heaps, 30,000 tons per day of high-grade oxide ore is treated in crushed (12 mm) conveyor-stacked heaps and 12,000 tons per day of unoxidized ore is treated in a processing plant (gravity separation followed by leaching in stirred tanks).

2.1.3. *Oxidized massive sulfides*

The oxide zone of massive sulfide ore deposits may contain gold and silver in iron oxides. Typically these are very soft and permeable, so crushing below 75 mm often does not increase heap-leach recovery. The Filon Sur orebody at Tharsis, Spain (Lion Mining Company) and the Hassai Mine, Sudan (Ariab Mining Company) are successful examples of heap leaches on this type of ore. Because the ore is fine and soft, the ore is agglomerated using cement (Hassai uses 8 kg cement per tonne of ore), and stacking of the heaps is done using conveyor transport systems.

2.1.4. *Saprolites/laterites*

Volcanic- and intrusive-hosted orebodies in tropical climates typically have undergone intense weathering. The surface *cap* is usually a thin layer of *laterite* (hard iron oxide nodules). For several meters below the laterite, the ore is converted into *saprolite*, a very soft water-saturated clay sometimes containing gold in quartz veinlets. Silver is usually absent. These ores show the highest and most predictable recovery of all ore types, typically 92 to 95% gold recovery in laboratory tests, and 85% or greater in field production heaps. Ores must be agglomerated, and may require up to 40 kg of cement per tonne to make stable permeable agglomerates. Many of the West African and Central American heap leaches process this type of ore.

2.1.5. Clay-rich deposits

In some Carlin-type deposits, as well as in some volcanic-hosted deposits, clay deposition or clay alteration occurred along with gold deposition. The Buckhorn Mine, Nevada (Cominco, now closed), and the Barney's Canyon Mine, Utah (Kennecott), are good examples. These ores are processed using the same techniques as for saprolites, except that crushing is often necessary. Because of the mixture of soft wet clay and hard rock, a typical crushing circuit design for this type of ore is a single-stage impact crusher. Truck stacking almost always results in some loss of recovery. Agglomeration with cement may not be necessary, but conveyor stacking is usually employed.

Barney's Canyon employs belt agglomeration (mixing and consolidation of fines as it drops from conveyor belts) followed by conveyor stacking. The new La Quinua operation at Yanacocha employs belt agglomeration followed by truck stacking.

2.1.6. Silver-rich deposits

Nevada deposits contain varying amounts of silver, and the resulting bullion may assay anywhere from 95% gold, 5% silver to 99% silver, 1% gold. Silver leaches behave chemically similar to gold, although usually the per cent silver recovery is significantly less than that of gold. Examples of nearly pure silver heap-leaches are Coeur Rochester in Nevada, and Comco in Bolivia.

2.2. Climate extremes

The ideal heap-leach location is a temperate semi-arid desert location such as the western part of the USA. However, heap leaching has been successfully applied in a variety of climates:

- Illinois Creek, Alaska, and Brewery Creek, Yukon, are located near the Arctic Circle and experience temperatures of −30°C for several months per year.
- Several heap leaches are located in the high Andes of South America (Comco at Potosi, Bolivia; Yanacocha and Pierina, Peru; Refugio, Chile) at altitudes above 4,000 m (13,000 ft).
- At another extreme, Hassai, Sudan, is in the dry eastern Sahara fringes. This operation experiences normal daytime temperatures that routinely exceed 50°C in the summer, with annual rainfall of <20 mm. One of the advantages of heap leaching over conventional cyanide-leach plants and gravity-recovery plants is that heap leaching consumes very little water.

With good water management practices, water consumption can be <0.3 tonnes of water per tonne of ore.
- Several heap-leach operations are located in tropical wet climates, where rainfall may exceed 2.5 m/yr. This amount of water can be handled with good water management practices.

2.3. Heap permeability and flow efficiency

The key element in a successful heap-leach project is a heap with high and uniform permeability. In any heap there are four zones with different flow regimes:

- *coarse channels*, which allow direct short-circuiting of solution from top to bottom;
- *highly permeable zones*, in which solution is efficient at contacting the rock and washing the gold downward in *plug flow*;
- zones of *low to zero permeability*, where high-grade solution or unleached ore may be trapped, and
- *base drainage* layer.

If the heap were *ideal*, with solution moving in true plug flow, then when one displacement volume of solution was placed on top of the heap, it would fully replace the solution in the heap. This would equate to 100% wash efficiency. In practice, the 'best' heap leaches exhibit a wash efficiency of about 70%. The importance of choosing the correct ore stacking method cannot be underestimated. Similarly, it is very important to install an efficient drainage base of crushed rock and embedded perforated pipes below the heap.

2.4. Recovery delay in multiple lift heaps

As subsequent lifts are stacked, lower lifts are compressed and the percentage of low-permeability zones increases. The first solution exiting an upper lift may have a gold concentration of up to three times that of the ore. If impermeable zones have developed in a lower lift, high-grade solution may be trapped, causing a severe reduction in recovery rate and possibly in overall recovery percentage.

The highest heap leaches currently in operation are 120 m high, with about 10 lifts of ore. Hard ore, crushed or run-of-mine, can withstand the resulting pressure without significant permeability loss. Many softer ores can be agglomerated with enough cement so that they can perform under a load of 30 m, and in unusual cases up to 100 m. These properties can be properly evaluated in advance, in laboratory column tests which are run under design loads.

The delay in recovery as lifts are added to the heap is partly a function of the impermeability of the lower lifts, and partly a function of the wash efficiency discussed earlier. The net effect is that average recovery is delayed as the heaps get higher, some recovery is permanently lost, and overall pregnant solution grade decreases. Single-lift heaps 10 m high are justified where the grade of ore is high (above 1.5 g/t), and where the topography allows it.

2.5. Solution application rate, cyanide strength and leach time

The timing of gold recovery from ore in a heap leach is a function of five factors:

- The *rate of gold dissolution*. Coarse gold particles dissolve very slowly, and may not fully dissolve for several months in a heap-leach environment.
- The percentage of gold that exists as *free or exposed* particles.
- The *rate of diffusion* of the cyanide solution into rock fractures, and of gold cyanide back out of the rock fractures. Where the gold occurs on tight fractures or in unfractured rock, the rock must be crushed into fine particles to achieve target rates and levels of recovery.
- The effect of *chemical reactions* within the heap, or within rock particles, which destroy cyanide and alkalinity or which consume oxygen.
- The *rate of washing* of gold off the rock surfaces and out of the lift of ore under leach. This is a complex issue, which depends on the overall permeability of the lift and the local permeability variations due to segregation and compaction as the lift is being constructed.

The above factors cause wide theoretical differences in response of various ores to leaching. However, in practice, most heap-leach operations apply solution to crushed-ore heaps within a fairly narrow range of flows, typically (8 to 11 L/h/m^2 (0.035 to 0.048 gpm/sq.ft). Most gold heap leaches apply cyanide within a range of 200–600 mg/L NaCN. Silver-bearing ores should usually be leached with a cyanide level of 600 to 1000 mg/L NaCN.

3. DESIGN FOR AMBIENT WEATHER CONDITIONS

3.1. Laboratory testing and control

As with any processing method, it is very important to base the design on the results of a comprehensive programme of laboratory testing. For a heap leach, the key parameters that are defined in the laboratory are crush size, heap stability, permeability versus heap height, cyanide strength and consumption, the need for agglomeration and the amount of agglomerating agent (usually Portland cement) required, leach time, and per cent recovery. Derivative parameters such as the height of individual lifts and the method of stacking are also determined.

Heap leaching has inherent risks that can be largely eliminated if the operating practices follow the results of initial and ongoing laboratory testing. The risks result from the nature of the operation. The results of the process are usually not known for several weeks or months after the ore is stacked, and at this point it is not economical to reprocess the ore. Mistakes made in the initial plant design or operating practices, for instance by not crushing finely enough, or by not agglomerating or stacking properly, can result in cash-flow problems that might persist for up to a year after the problem is solved.

3.2. Design for temperature extremes

High ambient temperature is not a direct problem. In very hot desert areas where drip irrigation is used, sunlight will significantly heat the solution. Even then, because of the effect of cool nighttime temperatures, it is unusual to see heap effluent solution temperatures above 15°C. Hot leach solutions dissolve less oxygen than cold solutions and this can affect the rate of gold recovery in oxygen-starved heaps. However, usually there is sufficient oxygen present, and the higher overall activity due to the higher temperature more than offsets the oxygen effect.

Low temperature can be a problem. Many Nevada heap leaches report a significant recovery decrease in winter, which is offset the following summer. When a cold weather project is anticipated, column tests should be run under cold conditions. There are several reasons for a reduction in recovery rate with lower temperatures:

- Rate of reaction is slowed as solution temperature approaches freezing. Comparative laboratory column tests show that recovery rate drops significantly when the heap temperature drops below 5°C. Solution viscosity increases significantly as temperature drops. This affects both the heap and the process plant.
- Solution flowing slowly through the normally unsaturated heaps flows via the meniscus on the surface of particles, and the thickness of this meniscus is a direct function of viscosity. Viscosity of water decreases from about 1.20 cP at 15°C to 0.66 cP at 40°C. For this reason, cold heaps tie up more process solution (and hence, more gold inventory) than warm heaps.

3.3. Water balance

Since many heap leach operations occur in desert areas where water is scarce, and others occur in environmentally sensitive areas where water discharge is not acceptable, the balance between water collection and evaporation is important. Fortunately, by adjusting the method and scheduling of solution application, it is usually possible to meet the local requirements.

Evaporation of water, regardless of its mechanism, requires a heat input of 580 kcal/L (8300 BTU/US gallon) of water evaporated. A heap leach gets this heat input from three sources: direct solar heating on heap and water surfaces; latent heat in the shroud of air within the *sprinkler envelope*; and latent heat in the air that is pulled through the heap by convection.

Average 24-h incident solar radiation on a flat horizontal surface ranges from 840 kcal/L (12,000 BTU/sq.m/day) in the central USA to about 2,100 kcal/L (30,000 BTU/sq.m/day) in equatorial desert conditions, which could theoretically evaporate 5 to 12 L of solution per day. With a typical heap application rate of 10 L/m^2/h, incident solar radiation could account for an evaporation rate of 2 to 5% of applied solution when using sprinklers. Evaporation would be somewhat less when using drip irrigation (1 to 4%) because some of the solar energy is re-radiated from dry areas on top of the heap. This same heat input would result in pond evaporation of 5–13 mm/day.

Use of sprinklers rather than drips may result in the loss of up to 30% of solution pumped. This is because the sprinkler droplets trace an arc through a shroud of air, which is very seldom at 100% humidity. A gentle breeze of 3 km (2 miles) per hour will replace the *saturated shroud* on a typical 500-m-long heap with unsaturated air every 10 min, and the pumping action of the sprinkler droplets will cause additional rapid air replacement. A good discussion of evaporative sprinkler losses is presented in *University of Florida Cooperative Extension Service Bulletin 290*. Typical sprinkler evaporation at operations using coarse-drop sprinklers in Nevada-type climates (arid, temperate) is up to 15% of solution pumped on summer days and 2–4% on summer nights, averaging about 7% annually.

Overall evaporative losses include the sprinkler losses, convective loss from air flowing through the heap and losses due to heating/evaporation from ponds and from other areas not sprinkled. These have been determined at several Nevada operations to be up to 20% of total solution pumped in summer months and 10% annually. Thus, direct sprinkler loss accounts for about 60% of the total. Use of drip irrigation can reduce but not eliminate evaporative loss.

In tropical climates, noticeable losses occur even during the rainy season. KCA's in-house experience on several tropical heap-leach projects where rainfall is seasonal and up to 2.5 m/y, is that overall annual evaporative loss from all sources, when using wobbler-type sprinklers operated 24 h/d, is about 7% of solution pumped. Typical heap application rate is 10 L/h/m^2, or 88 m/yr (9 in./day). Thus, evaporative loss of 7% is equal to 6.2 m/yr on the areas actually being sprinkled. If the heap and pond systems are properly designed, the active leaching area can be up to 40% of the total area collecting rainfall; it is therefore possible to operate in water balance when rainfall is 2.5 m/yr. For these operations, very large solution surge ponds are required: at Sansu, Ashanti, Ghana (rainfall 2.5 m/yr), for a 3,000 t/d heap leach, total pond volume was 60,000 m^3.

In West Africa and Central America it is often acceptable practice to treat and discharge excess solution during the rainy season. Typically, excess process solution is routed through a series of ponds where cyanide is destroyed using calcium hypochlorite or hydrogen peroxide, followed by adjustment of pH to near neutral values. The SO_2/air system, using copper-catalysed hyposulfite to destroy cyanide, can also be employed for this purpose. Cyanide-free solution may be further treated in controlled wetlands (swamps) to remove heavy metals prior to discharge.

The worst water-balance situation occurs in cool, damp climates such as high-altitude operations (for instance the Landusky-Zortman operation in Montana, now closed). In such climates, rainfall and snowfall may be significant and evaporation is minimal. Generally, such heaps can stay in water balance with an aggressive program of summer sprinkling. Arctic heap leaches (Brewery Creek, Yukon; Illinois Creek, Alaska) have been able to stay in water balance because precipitation is lower than the total water requirement needed to saturate the ore.

3.4. Solution application equipment

A variety of solution application methods have been employed, but for mainstream heap leaches either drip emitters or wobbler sprinklers are used:

- *Drip emitters*, which issue drops of water from holes every 0.5–1.5 m across the heap surface, are very common. Drip emitters are easy to maintain, and they minimize evaporation. The main drawback to drip emitters is that they do not provide continuous drip coverage. Thus the top 1 m of the heap may not be leached very well until it is covered with the next lift. Other problems are that emitters require an intense (and expensive) use of anti-scalant, and they require the use of in-line filters.
- *Wobbler sprinklers* are used at a large number of operations. Their main advantages (compared with drip emitters) are that they spray droplets into the air so that evaporation can occur, and also deliver a uniform solution distribution pattern, which ensures uniform leaching of the heap surface. Wobblers are typically placed on a 6 × 6 m pattern across the heap surface.

All currently operating tropical-climate heap leaches employ wobblers to control water balance.

- A disadvantage of all sprinklers is that they require continual servicing, and personnel spend extended periods working in a 'rainstorm'. Occasional skin contact with mild cyanide solution does not necessarily pose a health problem, but an environment that encourages repeated skin/solution contact is not recommended. Sprinkler maintenance personnel wear full rain gear to eliminate any exposure problem, but the working environment (especially in cold weather) can be harsher than with drip emitters.

Regardless of the systems used for solution application and management, capital and operating costs for solution handling are usually small. Total installed piping cost including header pipes is about US\$0.60/m^2, or US\$0.05/tonne of ore leached.

For the average two-cycle leach, 2 tonnes of solution are pumped to the heap and 1 tonne to the recovery plant, for each tonne of ore leached. Typically on-heap pressure for pumping barren solution is ~700 kPa (100 psi) at the pumps, and in-plant pressure for pumping pregnant solution is ~200 kPa (30 psi). Thus, for 2 tonnes of solution per tonne of ore, power for pumping is 1.8 kWh/t of ore and cost is US\$0.14/t. Where heaps are very high or where evaporation is required, power consumption can approach 4.0 kWh/t.

3.5. Leach pads and ponds

The leach pad below the heap is a significant element of a heap leach design. The ideal location for the heap is a nearly flat (1% slope), featureless ground surface. Usually some earthwork is required to modify contours, but it is not necessary to eliminate all undulations. It is only necessary that all solution will flow across the surface towards collection ditches on the base or sides of the heap. Where the slope exceeds 3%, the front edge of the heap (30–50 m) should be graded flat to provide a buttress to prevent heap failure. Heaps can be placed in fairly steep-walled valleys with side slopes up to 20% (12°).

3.6. Valley fill heap leach

A *valley-fill* heap-leach is a heap leach that has been built upslope from an earth dam. The containment area of the dam is filled with the stacked ore. The voids in the ore provide solution containment, and this volume serves as the pregnant solution storage pond. The ore stacked in the containment area behind the dam is usually a small part of the heap, which continues upslope and above the containment area. Valley-fill heap-leaches are used where terrain is steep and the ore must be placed in a narrow valley. They are also employed in arctic or high-altitude environments as a method of keeping the process solution from freezing.

3.7. Pad construction cost

The costs shown in Table 1 are typical installed cost (in 2004 US$) per square metre of pad surface for a padsite requiring minimum preparation. If complicated earthworks are required, these may add up to \$5.00/m^2 to the costs shown.

Ponds are installed downslope from the heap to provide storage of process solution. Usually there is a pregnant solution pond, a barren solution pond, and an overflow/storm-water pond. There may be one or more intermediate solution ponds (sometimes solution is recycled from older to newer heaps to build up the gold content before processing).

Ponds are sized to permit storage of sufficient process solution so that the operators do not have to closely watch the pond levels. In addition to this ‘operating capacity’, ponds are sized to contain solution during a several-day power outage and a major rainstorm event. Pond construction is similar to leach-pad construction, except that there is usually a second plastic liner with leak detection between the liners.

3.8. Mining, ore preparation and stacking

Mining of ore for heap leaching employs the same techniques and equipment as mining of ore to feed any other process method. Where uncrushed ore (run-of-mine (ROM) ore) is placed on the leach pad, ore may be blasted very heavily in order to reduce rock size and improve gold recovery. In high-rainfall environments when processing clay-rich material, it is very important to practice a mining routine that minimizes the amount of rainfall absorbed by the ore.

Ore preparation varies widely. ROM ore may be hauled from the mine and dumped directly onto the heap. At the other extreme from ROM leaches, Comsur’s Comco silver heap leach at Potosi in Bolivia crushes and then dry grinds all ore prior to agglomeration, with a grind size of 50% passing 150 μm (100 mesh). Three operations (Ruby Hill, Barney’s Canyon and Castle Mountain) grind high-grade ore and reblend it with the ore stream going to the heap leach (at Ruby Hill and Castle Mountain, the high grade is leached in agitated tanks to partially recover the gold).

Ores high in clay (such as saprolites) are typically processed by two stages of crushing using toothed roll-crushers, then agglomerated in drums and stacked using a conveyor stacking system. Many ores are crushed and then either truck-stacked or conveyor-stacked without agglomeration. For these harder ores, crushing is usually done using a jaw crusher followed by one or two stages of cone crushing.

Table 1
Leach pad component costs

Construction element	Cost (US\$/m^2)
Preliminary earthworks – removal of topsoil, building of edge *berms* and collection ditches. Cost assumes minimal alterations to topography. Sometimes it is necessary to do extensive site preparation, at a cost of several dollars per square meter	\$1.00
150–300 mm of compacted clay-rich soil, engineered to a permeability of 10^{-6} cm/s	\$1.00–\$3.00
Limited leak detection, usually embedded small-diameter perforated pipes placed near the lower edge of the heap and in areas of solution concentration. These daylight to collection sumps at the front of the heap. Leakage is usually permitted up to a certain small limit provided that the area is not extremely environmentally sensitive	\$0.50
Plastic liner, usually 0.75–1.00 mm (30–40 mil) thick PVC, or 1.50–2.00 mm thick HDPE or LLDPE. The liner is delivered in rolls up to 2000 m^2 each, and field-welded to form the total liner. The initial installation for a 'small' heap leach may cover 100,000 m^2; large installations may install 500,000 m^2 each year. An HDPE liner of 2.00 mm thickness has sufficient strength and puncture resistance to support a heap up to 150 m high	\$3.00–\$5.50
Geotextile cover may be placed above the plastic to prevent damage of the plastic by rocks in the drainage layer. The use of the geotextile is an economic tradeoff with the crush size of the gravel	\$1.50
Drain pipes, usually 75–100 mm perforated flexible tubing, are placed on 6-m centres above the plastic. Where solution does not drain directly out the front of the heap, large collector pipes may also be embedded in the drainage layer	\$0.50
Gravel cover, up to 1000 mm thick, is placed next to protect the pipes and the liner, and to provide a permeable base below the heap. Cost may be low if the gravel can be produced from the ore	\$0.50–\$5.00
Total installed pad cost	\$8.00–\$17.00

3.8.1. Agglomeration

The term *agglomeration* means different things to different operators.

- At the simplest level, the ore is hard but contains a large percentage of fines. *Agglomeration* means simply wetting the ore with water so that the fines stick to the coarse particles and do not segregate as the heap is built.
- At the next level, the ore contains amounts of clay or fines that begin to plug a heap of untreated ore. *Belt agglomeration* may be employed. In this technique, cement and water are mixed with the ore at a series of conveyor drop points, and the mixture tends to coat the larger rock-particles. The primary goal is stabilization by mixing and contact. A typical conveyor stacking system involves ten or more drop points, so belt agglomeration may occur as a normal part of the process.
- Where ores are nearly pure clays, such as the laterite/saprolite ores in tropical climates, *drum agglomeration* is usually employed. The ore is first crushed finely enough (typically 25–75 mm) to form particles that can be a stable nucleus for round pellets. Cement and water are then added and the ore is sent through a rolling drum. The fines and the cement form a high-cement shell around the larger particles, and the rolling action of the drum compacts and strengthens the shell. Drum size and throughput are a function of several factors, but typically a 3.7-m-diameter, 10-m-long drum can process 750 tonnes of ore per hour. A 2.5-m-diameter drum can process 250 t/h. At the Tarkwa mine in Ghana, two 3.7 m drums are installed to process up to 20,000 tonnes ore per day.

3.8.2. Truck stacking

Where rock is hard and contains very little clay, it is possible to maintain high permeability even when ore is crushed and dumped with trucks. Truck dumping causes segregation of the ore – the fines remain on the top surface and the coarse material rolls to the base of the lift, creating a highly permeable zone at the base.

Truck stacking can also result in compaction of roadways on top of the heap. Several studies have indicated large trucks noticeably compact ore to a depth of 2 m. To mitigate this problem, most operations rip the ore after stacking (but prior to leaching).

Stacking the ore with trucks can result in the tie-up of a large tonnage of ore below the truck roadways. This is a bigger problem on small operations than on large ones, because the roadway width is nearly the same regardless of the daily production rate. For a heap leach of 5000 t/d, the roadways on the heap can tie up one month's ore production, with a value of US$1.8

million. A conveyor system that stacks ore from the base of the lift can reduce unleached inventory to a few days' production. Because of this inventory reduction, at smaller operations where the ore is crushed, it is usually less capital-intensive to install a conveyor stacking system. For operations of 100,000 t/d, truck stacking is more flexible and may be less capital intensive than a conveyor system.

3.8.3. Conveyor stacking

Conveyor stacking systems commonly include the following equipment:

- One or more long (overland) conveyors that transport the ore from the preparation plant to the heap. Typically, these consist of conveyors up to 150 m long. At Tarkwa, Ghana, a 3 km overland conveyor is used.
- A series of 8–15 *grasshopper* conveyors to transport the ore across the active heap area. Grasshoppers are inclined conveyors 20–30 m long, with a tail skid and a set of wheels located near the balance point.
- A transverse conveyor to feed the stacker-follower conveyor.
- A stacker-follower conveyor, typically a horizontal mobile conveyor that retracts behind the stacker.
- A radial stacker 25–50 m long, with a retractable 10 m conveyor at its tip.
- Wheels, discharge angle, and stinger position are all motorized and are moved continuously by the operator as the heap is built.

The typical cost of a complete stacker system with a 900 mm (36 in.) wide belt for a 10,000 t/d heap-leach operation, including the stacker and follower conveyors, and ten grasshopper conveyors, is US$1.5 million (delivered and installed at a typical developing-country heap leach site). Three hundred metres of overland conveyor connecting the stacking system to the crusher/agglomeration system cost an additional US$500,000. (Fig. 3)

For operations stacking very high tonnages, large stackers can be mounted on caterpillar tracks to reduce ground pressure. Rahco International, Inc. (Spokane, Washington, DC) makes a unique stacker, which is ideally suited to building large heaps at high tonnage rates. The stacker, shown in Fig. 4, has individual drive adjustments so that it can climb up ramps to the next level and make sharp radius turns.

3.9. Recovery of gold and silver from heap-leach solutions

Gold and silver can be recovered from solution by contacting the solution with granular activated carbon in columns (CIC), followed by stripping of the carbon using a hot caustic solution. This caustic solution is processed in electrolytic cells or in a zinc dust precipitation vat to recover the metal, which is then melted to produce a doré (impure bullion) bar. A CIC plant is shown

Fig. 3. Stacking system for capacity of 10,000 tonnes ore per day. Elements include stacker with extendable stinger; follower conveyor; cross conveyor; and several grasshopper conveyors.

Fig. 4. Rahco stacker building a 12 m lift by tripping the ore over the advancing edge. The stacker can climb ramps and turn sharply to fit project requirements.

in Fig. 5. Where the ore is high in silver, typically with a recoverable silver content of more than 10 g/t (0.3 oz/ton) of ore, Merrill-Crowe zinc precipitation is used instead of carbon adsorption. In this process the solution is clarified and de-aerated, then contacted with zinc dust to precipitate metallic gold and silver. This precipitate is then melted to produce bullion.

Fig. 5. Five-stage carbon adsorption column plant (CIC plant) built by Kappes, Cassiday & Associates for Glamis Gold's San Martin, Honduras project. There are two parallel column trains (one is behind the other in this view). The plant can process up to 900 m^3 of solution per hour, and is sized for an operation that processes up to 20,000 tonnes of ore per day.

3.10. Design considerations for reclamation and closure

Once the heap-leaching operation is completed, the facility must be closed in accordance with local environmental requirements. Closure activities are highly variable, depending on the environmental sensitivity of the site and on the regulatory regime. In general, heaps are washed for a short period of time (commonly 3 years), during which time 1 tonne of wash water or recycled treated process solution is applied. Heaps are then capped, and ponds are filled and capped.

Regulators are recognizing that a better approach than thoroughly washing the heap is to conduct a 'limited' washing program and then to cap the heap with a clay cover and/or an *evapo-transpiration* cover of breathable soil with an active growth of biomass. These covers are designed to prevent infiltration of water into the heap. After several years of active closure activities, the flowrate of the heap effluent decreases to a manageable level (or to zero in arid environments). A relatively small *cash perpetuity bond* is maintained, such that the interest on the bond covers the cost of maintaining and operating the intermittent pumping facility as long as is necessary.

A 2 million tonne heap of ore covering 90,000 m^2 (average thickness 14 m), located at Goldfield, Nevada, was recently closed with a clay/soil cap. Heap effluent gradually and steadily declined to 2.0 L/min after 36 months. In subsequent years, heap effluent declined about 30% per year. Periods of intense above-average rainfall did not affect effluent rate. While this is a small and not very high heap, scale-up of these data should be applicable for preliminary design purposes.

Worldwide practice ranges from simple washing and abandonment, to the more complex procedure described above. Environmental design is an industry unto itself, and the simplistic concepts discussed here may not be applicable in other situations. Heap closure needs to be addressed in the feasibility stage of the project. Typical cost of closure, including three years of heap washing, is US$0.50/tonne of ore stacked. See Chapters 10 and 11 for more information on plant and tailings dam closure.

3.11. Capital cost

Capital cost for a small 'basic' heap leach (3,000 t/d) with minimal infrastructure at a developing-country leach site is typically $3,500 to $5,000 per daily tonne of ore treated, with the higher cost attributed to high logistics expenses at remote sites such as central Asia. Larger operations (15,000–30,000 t/d) cost $2,000–$4,000 per daily tonne, but may commonly reach $6,000 where 'corporate culture' calls for process redundancy and infrastructure. Use of a mining contractor and/or a crushing contractor is common, and may eliminate the capital costs for these line items.

Capital cost breakdown is shown in Table 2 for 'typical' developing country, remote sites with minimal infrastructure and minimal redundancy. Each operation, of course, will have a unique mix of capital cost line items.

3.12. Operating cost

Operating cost is not very sensitive to the size of operation. Published direct cash operating cost for Barrick's Pierina mine (85,000 t/d) is US$3.93/t, including $0.87 for mining. A recent study of an on-going operation in Africa concluded that increasing production from 4,300 to 13,000 t/d would decrease costs (excluding mining) from $5.80/t to $5.10/t.

Average operating costs for 'typical' heap leaches can be broken down as shown in Table 3. Costs are shown for ores that need crushing, agglomerating and conveyor stacking. Not all items in the list are appropriate for all operations; the right-hand column shows costs that are more typical of a 30,000 t/d, coarse-crushed, unagglomerated Nevada heap leach.

4. CONCLUSIONS

Although the concepts of precious-metal heap leaching are simple, the practices have substantially evolved over the past 35 years. Early choices for pad materials, sprinkling systems, and stacker designs have been discarded under the pressure of operating experience and cost-reduction factors. Overall operating costs have continually declined as 'superfluous' activities and controls have been eliminated.

Table 2
Heap-leach capital costs

Cost element	Cost at 3,000 t/d (US$)	Cost at 15,000 t/d (US$)
Feasibility/design studies/permitting	400,000	1,000,000
Mine equipment	2,200,000	9,900,000
Mine development	600,000	1,200,000
Crushing plant (two-stage)	1,200,000	3,500,000
Leach pads/ponds	1,000,000	4,600,000
Agglomeration/stacking system	1,000,000	3,500,000
Process pumps, plant, solution distribution piping	1,100,000	3,500,000
Laboratory	300,000	500,000
Infrastructure (power, water, access roads, site office and service facilities)	1,700,000	7,500,000
Owner's pre-production cost	700,000	2,800,000
EPCM (engineering, procurement, construction management)	900,000	2,000,000
Import duties/IVA	800,000	7,000,000
Equipment/materials transport	600,000	2,100,000
Initial operating supplies	300,000	1,500,000
Working Capital	1,200,000	3,000,000
TOTAL	14,000,000	53,600,000
Capital cost per daily tonne (US$/t)	4,700	3,600

In spite of the apparent simplicity of the heap-leach process – or perhaps because of it-there were many failures in the early years. There is now a large resource of successful operations from which to draw the experience needed to optimize the process. Heap leaching is expected to maintain its place as one of the principal tools for extracting gold and silver from their ores for both large and small deposits. The challenge for the future will be to remember and apply the experiences of the past.

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Table 3
Typical heap leach operating costs (US$/t)

Cost element	3,000 t/d	15,000 t/d	30,000 t/d (typical Nevada)
Mining (strip ratio 2.5:1, cost/tonne of ore)	3.00	2.00	1.70
Crushing, primary	0.40	0.20	0.20
Crushing, second plus third stage	0.50	0.40	0.20
Crushing (fourth stage, to 1.7 mm (10 mesh))	0.80	0.80	−0.00
Agglomeration/stacking	0.20	0.10	0.10
Leach operations (including sprinkler supplies)	0.50	0.30	0.20
Recovery plant operations	1.50	1.30	1.40
General site maintenance	0.60	0.30	0.30
Cement for agglomeration (10 kg/t)	1.00	1.00	−0.00
Cyanide, lime, other reagents	0.30	0.30	0.30
Environmental reclamation and closure	0.50	0.50	0.50
General and administrative, support expenses	1.50	0.50	0.30
Total site cash operating cost	10.80	7.70	5.20

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Closely held affiliates of *Kappes*, *Cassiday & Associates* include *KCA Steel Services LLC*, which provides structural steel fabrication and erection in the Reno area, and *Decommissioning Services LLC*, which provides mine closure management services.*KCA* has built and installed 35 modular plants for the processing of gold and silver ores using the processes of carbon adsorption/electrowinning or zinc precipitation. In a typical year, the company provides services for over 100 projects and is involved in a major way in 4–6 startups.

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Chapter 20

Advances in the cyanidation of gold

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1. INTRODUCTION

In the last 15 years, most of the development in the cyanidation of gold has occurred in response to the decreasing grade of deposits, the shift from surface mining to underground mining, the increasing complexity of treatment and the concern for environmental constraints. Research has focused on the optimization of reagent addition (*e.g.* cyanide, oxygen and lead nitrate) and on metallurgical strategies to measure and control these parameters, as well as in the areas of equipment and automation. Efforts to introduce online cyanide analysers were made in the late 1980s; however, progress was slow. The analysers required additional testing to be reliable and effective and to yield more accurate titration results. Online dissolved oxygen sensors were integrated in the late 1980s simultaneously with oxygen addition and various injection devices.

Sulfide in gold ores not only consumes oxygen and cyanide but also forms a coating on gold grains. This passive layer reduces gold-leaching kinetics and overall extraction. Improvement of lead nitrate addition strategy has made it possible to minimize gold passivation.

This chapter highlights the latest developments in cyanidation of gold, as well as plant improvements and associated research aspects in terms of gold-leaching kinetics and surface passivation.

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2. MECHANISM OF CYANIDATION

2.1. Chemistry and electrochemistry

The most commonly used equation for the dissolution of gold in a cyanide solution, known as Elsner's equation, is

$$4Au + 8NaCN + O_2 + 2H_2O \Rightarrow 4NaAu(CN)_2 + 4NaOH \quad (1)$$

Gold dissolution is an electrochemical reaction in which oxygen takes up electrons at one part of the metallic surface (the cathodic zone), while the metal gives them up at another (the anodic zone). According to this reaction, at low cyanide concentrations, the dissolution rate is a function of cyanide concentration. At high cyanide concentrations, the dissolution rate is a function of oxygen concentration.

Gold dissolution is a heterogeneous reaction that is controlled by the diffusion of both reacting species (O_2 and CN^-) through the Nernst boundary layer. The rate of metal dissolution increases linearly with increasing cyanide concentration until a maximum dissolution is reached, beyond which there is a slight retarding effect. The dissolution rate is normally mass-transport-controlled in cyanide solutions with an activation energy of 8–20 kJ/mol (Habashi, 1967). The formation of precipitates at the surface of gold grains is an important aspect that determines the shape of the leaching kinetics plot. This aspect will be discussed later in this chapter.

Two of the main advantages of cyanidation are the selectivity of free cyanide for gold dissolution and the extremely high stability of the cyanide complex as illustrated in Table 1.

To avoid hydrolysis of cyanide (Eq. (2)), leaching must be carried out under basic conditions:

$$CN^- + H_2O \Rightarrow HCN + OH^- \quad (2)$$

Table 1
Stability constant of some gold compounds after Marsden and House (1992)

Complex	Au(I), β_2
$Au(CN)_2^-$	2×10^{38}
$Au(S_2O_3)_2^{3-}$	5×10^{28}
$Au(CS(NH_2)_2)^+$	2×10^{23}
AuI_2^-	4×10^{19}
$Au(SCN)_2^-$	1.3×10^{17}
$AuBr_2^-$	1×10^{12}
$AuCl_2^-$	1×10^{9}

However, in saline water, such as in many cyanidation plants in Western Australia, gold-leaching is performed at a pH below 10 to reduce the high cost of lime under these buffering conditions. Hydrocyanic acid (HCN) is monitored above the tanks to address the health and safety aspects. While leaching occurs outdoors in hot climates, in colder climates, it is normally carried out indoors to minimize the effect of the reduced temperature. Consequently, tanks are located in buildings to minimize the retarding effect of cold temperatures.

Reactions kinetics are extremely important because most cyanidation plants operate at maximum throughput. Other factors affecting gold-leaching kinetics are grain size, galvanic effects, agitation speed, temperature, foreign ions, *cyanicides* and *preg-robbing*. Coarse gold is usually recovered by gravity prior to leaching.

Lead, mercury salts, bismuth and thallium ions (Guzman *et al.*, 2000) accelerate the rate of dissolution of gold. The addition of lead salts to cyanide solutions has already been a common practice (used for more than 60 years) aimed at counteracting the harmful effect of sulfides, while mercury, bismuth and thallium are not used because of their extremely high toxicity. Recent electrochemical studies have quantified and explained the accelerating effect of these ions (Jin *et al.*, 1998, 2002; Guzman *et al.*, 2000, Jeffrey and Ritchie, 2000; Sandenbergh and Miller, 2001).

The most common method used to control lead nitrate addition is based on the relationship between the gold content of the leach residue, the dissolved oxygen concentration and the free cyanide concentration of the leach solution. Because the lead concentration is always very low (<0.1 mg/L), it is consequently not possible to use the analysis of the dissolved lead to control its addition. Surface analysis of gold using X-ray photoelectron spectroscopy (XPS) indicated that lead precipitates at the surface of gold and sulfide minerals in various forms (Deschênes *et al.*, 2000).

The following reactions show that lead reacts with gold to form $AuPb_2$, $AuPb_3$ and metallic lead, which clearly accelerate the gold dissolution (Jin *et al.*, 1998). Metallic lead was also found on the gold surface. Its presence also depolarizes the reduction of oxygen:

$$2Pb(OH)_2 + 5Au + 8CN^- \rightarrow AuPb_2 + 4Au(CN)_2^- + 4OH^- \tag{3}$$

$$AuPb_2 + 2CN^- + 4OH^- \rightarrow Au(CN)_2^- + 2PbO + 2H_2O + 5e \tag{4}$$

$$2PbO + 5Au + 8CN^- + 2H_2O \rightarrow AuPb_2 + 4Au(CN)_2^- + 4OH^- \tag{5}$$

$$Pb(OH)_2 + 4Au + 4CN^- \rightarrow Au_2Pb + 2Au(CN)_2^- + 2OH^- \tag{6}$$

$$3Pb(OH)_2 + 7Au + 12CN^- \rightarrow AuPb_3 + 6Au(CN)_2^- + 6OH^- \tag{7}$$

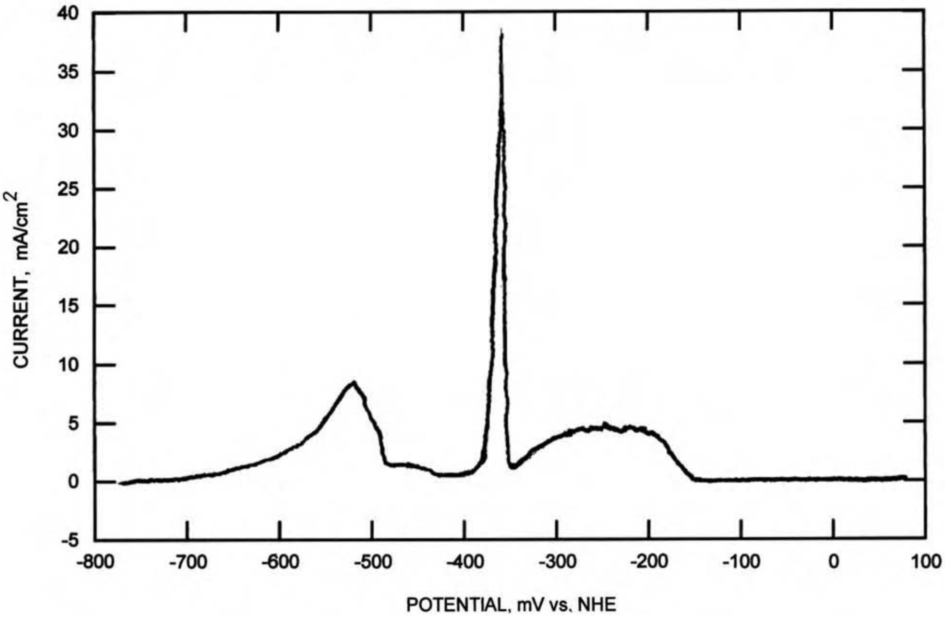

Fig. 1. Polarization curve for gold electrode treated with PbS in 1 M NaCN solution (Deschênes *et al.*, 2000).

Fig. 1 shows a potential sweep when the gold electrode is in contact with lead sulfide in a cyanide solution. The lead sulfide accelerated the gold dissolution rate most likely by the same mechanism as lead nitrate. The peak between −600 and −500 mV (vs. normal hydrogen electrode, NHE) corresponds to $AuPb_2$ alloy, the peak between −500 and −400 mV corresponds to $AuPb_3$ alloy, and the other two peaks correspond to the metallic lead phase. These three phases formed on the gold surface were observed by scanning electron microscopy – energy-dispersive spectrometry (SEM–EDS) and confirmed by X-ray diffractometry (XRD) (Deschênes *et al.*, 2000).

2.2. Reaction with sulfide minerals

Fig. 2 shows the effect of realgar [AsS], pyrrhotite [FeS], chalcopyrite [$CuFeS_2$], pyrite [FeS_2] and arsenopyrite [FeAsS] on gold-leaching (Deschênes *et al.*, 2002a). No detrimental impact of pulps containing 1.0% pyrite or 5.7% arsenopyrite was noticed. Pulps with 1.0% chalcopyrite, 1.2% pyrrhotite and 0.5% realgar produced significant reductions in gold-leaching kinetics. The negative effect was manifested in the following order: realgar > pyrrhotite > chalcopyrite. Leached sulfur from dissolving arsenopyrite and pyrite formed a partial layer of sulfide on exposed gold surfaces. At

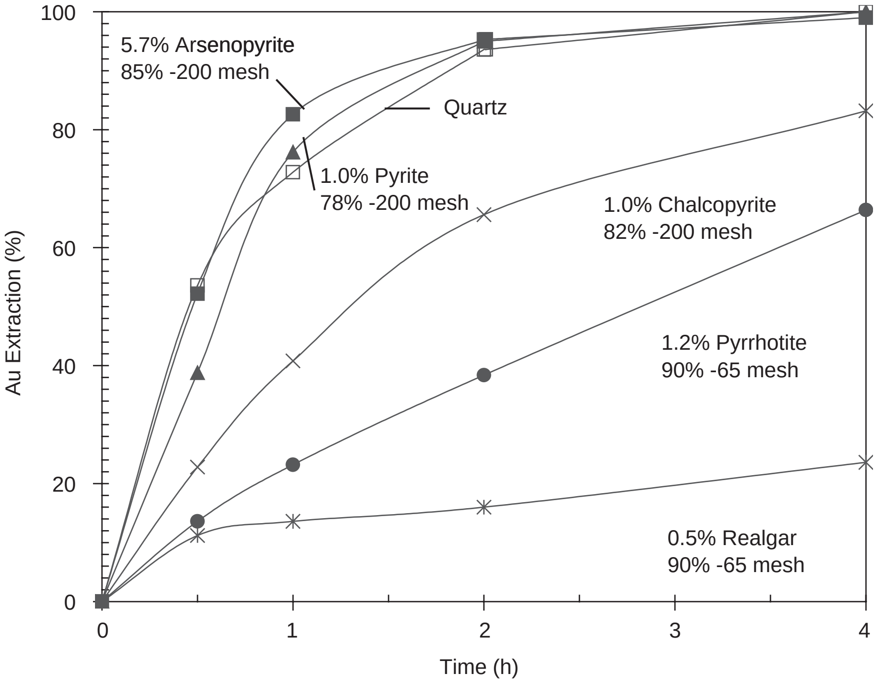

Fig. 2. Effect of sulfide mineral additions on gold-leaching (pH 11.5, 8 ppm O_2, 500 mg/L NaCN, Au: 25 g/t – after Deschênes, 2002a).

longer leaching times or higher mineral concentrations, arsenopyrite and pyrite were found to be detrimental to gold-leaching (Healey *et al.*, 2000).

The addition of lead nitrate resulted in a significant acceleration of gold dissolution kinetics, even in the presence of relatively high concentrations of realgar, pyrrhotite and chalcopyrite. Although oxygen effectively improved the leaching kinetics in the presence of sulfide minerals, it cannot replace lead nitrate in terms of efficiency. Oxygen was ineffective in terms of improving gold-leaching in the presence of realgar.

The XPS surface analysis showed that in the absence of lead, leaching reactions were impeded by precipitation of various compounds. Sulfide, silver, iron, calcium and lead were detected on the surface of gold in a slurry containing a pyrite concentrate (Fig. 3). The addition of lead nitrate significantly reduced or eliminated the amount of precipitates at the surface. It is possible that the sulfide species formed is a gold sulfide but additional work is required to verify this conclusion.

In the case of realgar, arsenic was detected in significant amounts on the surface of gold. Arsenic completely disappeared when lead nitrate was added.

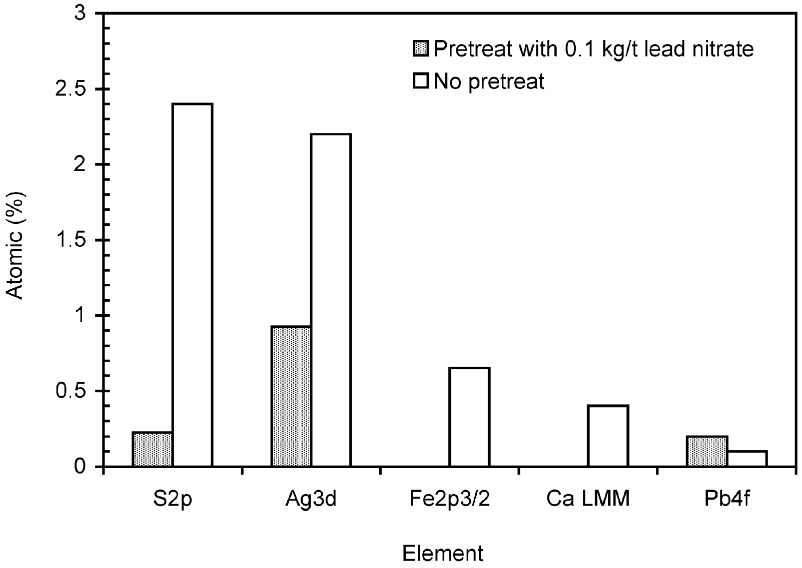

Fig. 3. Results of surface analysis of gold in contact with pyrite after conditioning with and without lead nitrate addition (after Guo *et al.*, 2004).

The gold surface had appreciable amounts of lead sulfide. The sulfur peak is broad and appears to indicate the presence of more than one type of sulfide.

The XPS examination showed that $Pb(OH)_2$ was still found on the pyrite, pyrrhotite and arsenopyrite particles. However, the chalcopyrite as well as the realgar particles showed no detectable amounts of lead. It is thought that lead hydroxide species have a passivating effect and decrease the reaction rate with cyanide (Deschênes *et al.*, 2000).

Stibnite, at levels as low as 20 g/t, significantly affects gold-leaching kinetics through the formation of a passivating film of Sb(V) oxide, possibly Sb_2O_5 (Guo *et al.*, 2004). This finding differs from previously published results (Hedley and Tabachnick, 1958), which reported the formation of thioantimonite, $HSbO_3^{2-}$. The detrimental effect of stibnite could be alleviated by maintaining a pH below 10 (to minimize stibnite dissolution) or by the addition of lead nitrate. The addition of oxygen to the slurry could have an even more negative effect on leaching rate. A summary of the XPS spectra (Fig. 4) shows the relative variations in the chemical species responsible for the formation of a passive layer on gold grains in a slurry with stibnite, for various conditions of pH and lead nitrate.

Passivation of gold by antimony can be alleviated by the addition of $Pb(NO_3)_2$ and/or lowering of pH. A high dissolved oxygen (DO) level did not show any positive effect on gold-leaching kinetics in the presence of Sb.

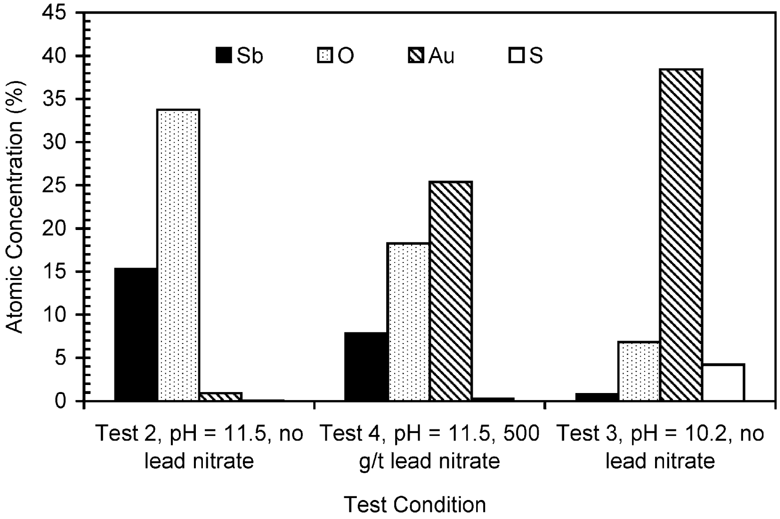

Fig. 4. Results of surface analysis of gold in contact with stibnite after conditioning for various pH and $Pb(NO_3)_2$ additions (Guo *et al.*, 2004).

The solubility of sulfide minerals was investigated half a century ago by Hedley and Tabachnick (1958). They found that the decreasing order of solubility for the most common sulfide minerals is pyrrhotite $\ggg$ marcasite $>$ pyrite. Arsenic and antimony minerals do not form stable cyanide complexes. The solubility of these minerals is a function of pH. At a pH value of 12, orpiment, stibnite and realgar dissolve significantly. At a pH value of 10, only orpiment dissolves appreciably. The relative order of reactivity of these minerals is stibnite $\ggg$ orpiment $>$ realgar $>$ arsenopyrite. Recent work on stibnite, arsenopyrite and realgar (Deschênes *et al.*, 2000; Guo *et al.*, 2004) obtained different findings than that obtained by Hedley. They found that arsenopyrite does not react to a noticeable extent in a cyanide solution. At a pH of 11.5, they found that realgar significantly interferes with gold-leaching. At levels as low as 0.1%, realgar reduced the gold-leaching kinetics by 40% in a 4-hour leach.

Yen and Aghamirian (2002) investigated the benefits of using a higher oxygen level in the pulp containing sulfide minerals and their dissolved ions. The study suggested that sulfide minerals could be divided into three groups depending upon their effect on gold-leaching: a group that has a negative effect (stibnite, chalcocite and pyrrhotite); a group that neither seriously reduces nor greatly enhances gold-leaching (pyrite, chalcopyrite, arsenopyrite and sphalerite); and, a group that improves gold-leaching (galena).

3. CONTROL STRATEGY FOR CYANIDE, OXYGEN AND LEAD NITRATE

3.1. Control of cyanide

The concentrations of cyanide used to dissolve gold in ores are typically much higher than the stoichiometric amount required, owing to the solubility of other minerals. Previous literature has indicated that higher levels of cyanide are related to the competition of other ionic species for cyanide (Marsden and House, 1992). This is one explanation, but it is not the only one. Additional cyanide is needed to counteract the retarding effect of the coating formed on gold grains by the dissolution of metallic sulfides. In addition, the leaching kinetics targeted must match the retention time of the circuit.

Three approaches have proved to be very efficient in reducing cyanide consumption in gold plants and reducing the cost of effluent treatment for cyanide destruction: the use of an online cyanide analyser, oxygen enrichment of the pulp and the addition of lead nitrate (or litharge). In the case of free-milling gold ores with little or no sulfide content, a low cyanide concentration is used (90–150 mg/L NaCN) (Deschênes and Putz, 1995). Consequently, the financial advantage of using an online cyanide analyser is usually not attractive.

Leaching of metallic sulfides requires higher cyanide concentrations. Copper sulfides usually generate higher cyanide consumptions than iron sulfides. Cyanidation of gold ores with copper minerals is discussed in detail in Chapter 32. An interesting methodology, using thermodynamic constants and solution analysis, was proposed to explain the deportment of cyanide in gold plant liquors and solids (Adams, 2001). The speciation of cyanide with metals and the formation of thiocyanate are part of the approach.

The CYANOSTAT was the first commercial online cyanide titrator installed. The Golden Giant Mine was operating a CYANOSTAT at the end of the 1980s. At the same period, the Zelweiger analyser was in common use in Australia in locations such as Mt Morgan and KCGM (Ellis, 2004). Use of the CYANOSTAT was halted after a few years because it was found to be unreliable. An Australian version, based on the same principle (*i.e.* spectrophotometry), and called the Alkay Analyser (Kaye and Jackson, 1991) was no more successful. The CYANCOR and the Cyanochem online analysers were the next generation of automatic titrators introduced and used on a continuous basis in Canada (Dufresne *et al*., 1994; McMullen *et al*., 1999). Cyanide titration is performed with silver nitrate and is based on a potentiometric end point. A similar prototype, called Chemtronics, was commercialized in Australia (Hyde, 1995).

Numerous problems had to be solved to keep these instruments online. While most of the difficulties associated with the sampling system were solved during the CYANOSTAT implementation phase, other problems had to be addressed, including robustness, reliability, corrosion resistance, maintenance and automation of sampling. The variation of the solution composition made the interpretation of results complex. It was also necessary to develop an automated cyanide addition strategy that would include the integration of the cyanide sensor.

Initial project results have indicated that the payback of online cyanide analysers is high. Because the cost of cyanide is typically a major expense for many gold operations, a 10% reduction in consumption represents significant savings. The use of the CYANCOR at Yvan Vézina plant (Dufresne *et al.*, 1994) and the Cyanochem at East-Malartic Division (McMullen *et al.*, 1999) resulted in up to 40% reduction in cyanide consumption. Fig. 5 illustrates the decrease in cyanide consumption over time for Yvan Vézina leaching circuit. The stabilization of cyanide concentration (Fig. 6) and the resultant reduction in usage rates translate into improved plant performance. Simultaneously, the extraction of gold was increased by 1.7%. It should also be pointed out that modifications in the metallurgical practices included the addition of lead nitrate.

Many factors have delayed the adoption of this new technology, including the ease of manual titration of free cyanide, the capital requirements

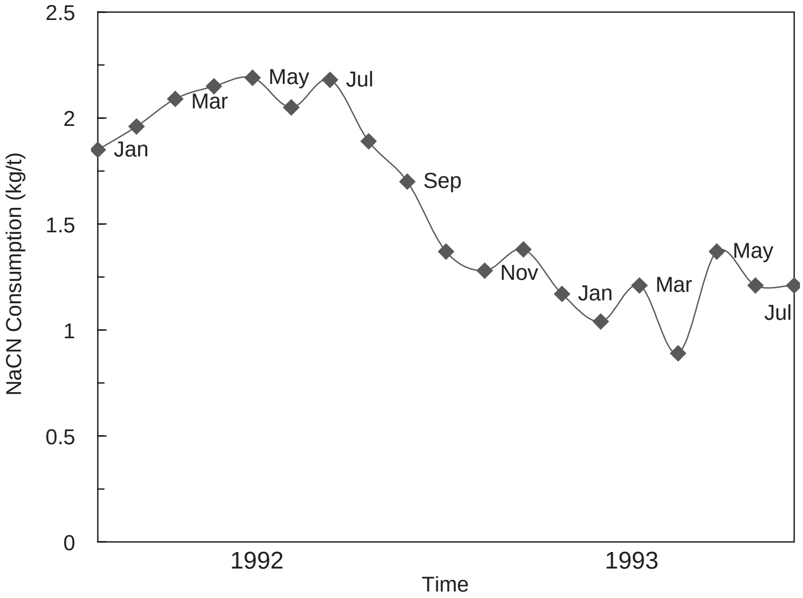

Fig. 5. Effect of online cyanide analysis on sodium cyanide addition at Yvan Vézina Plant (Dufresne *et al.*, 1994).

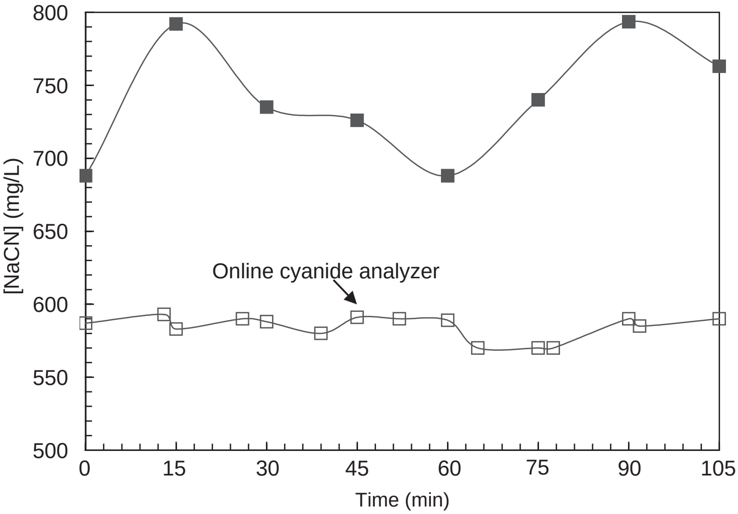

Fig. 6. Variation in free cyanide concentration at Yvan Vézina Plant before and after the installation of an online cyanide analyser (Dufresne *et al*., 1994).

associated with the installation of an on-stream cyanide analyser in the plant, and its lack of reliability and labour requirements.

Reports of successful implementations and pressure to reduce operating costs have contributed to a wider use of online cyanide analysis. Analysers that have been installed over the past 5 years at Dome Mine, New Britannia Mine, and Musselwhite Mine have contributed to a reduction in cyanide consumption. It is estimated that about 30% of Canadian gold plants use online cyanide measurement (Deschênes and Putz, 1999). Among Australian plants, this number is estimated to be about 50%. Improvements in the design of on-stream equipment have contributed to the development of more sophisticated cyanide-addition controls.

3.2. Oxygen

Elsner's equation shows that oxygen is critical for the dissolution of gold. The maximum dissolved oxygen content of a dilute cyanide solution is 8.2 ppm with the injection of air at 25°C. Conventional cyanidation is usually performed at a pH higher than 10 and an O_2 concentration greater than 6 ppm. If the concentration of dissolved oxygen drops below 4 ppm, gold dissolution rates are greatly reduced. On the other hand, the rate of gold dissolution will increase markedly as the concentration of dissolved oxygen rises above 10 ppm. An oxygen-enriched operation is one that is conducted at 12–18 ppm O_2 by sparging oxygen into the slurry. This implies that plant throughput can be increased by using a higher dissolved oxygen content. In the case of cyanidation plants processing gold ores with metallic sulfides, oxygen is not only used to optimize plant throughput but also to enhance gold extraction.

Because the dissolution of sulfide minerals consumes oxygen (Reactions (8), (10) and (11)), it is important to avoid a reduction in the gold-leaching rate associated with low dissolved oxygen in the pulp. Equation (9) is related to cyanide consumption and passivation of gold with sulfide:

$$2MS + 2(x+1)CN^- + O_2 + 2H_2O \Rightarrow 2M(CN)_x{}^{(2-x)-} + 2CNS^- + 4OH^- \quad (8)$$

$$MS + 2OH^- \Rightarrow M(OH)_2 + S^{2-} \quad (9)$$

$$2M(OH)_2 + 1/2O_2 + H_2O \Rightarrow 2M(OH)_3 \quad (10)$$

$$2S^{2-} + 2O_2 + H_2O \Rightarrow S_2O_3^{2-} + 2OH^- \quad (11)$$

Pure oxygen was first used to improve the cyanidation process by Air Products in South Africa in the 1980s (Stephens, 1988) and the practice was introduced in Canadian plants at about the same time (McMullen and Thompson, 1989). The Lac Minerals plants were the first operations to demonstrate the faster leaching kinetics associated with dissolved oxygen and lead nitrate. Use of oxygen-assisted leaching caught on quickly in the industry.

Fig. 7 illustrates the benefits of using a high oxygen content in cyanidation of a gold ore with low pyrite and pyrrhotite content (Deschênes *et al.*, 1999). A 16 ppm oxygen concentration in leaching can result in a faster dissolution

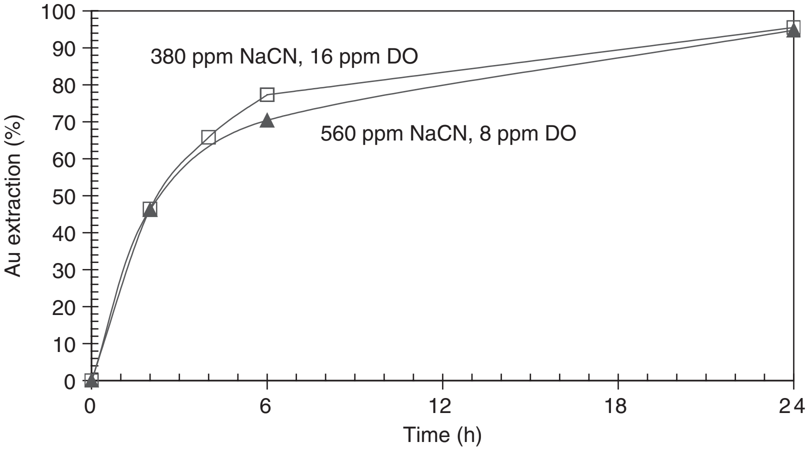

Fig. 7. Effect of oxygen and lead nitrate on gold-leaching kinetics of an ore containing pyrite and pyrrhotite at pH 11 (From Deschênes *et al.*, 1999. Reproduced with permission of MetSoc, CIM).

rate than a 147% increase in the cyanide concentration. The use of oxygen has resulted in a 30% reduction in the amount of cyanide required to reach such a leaching rate.

Technological advances improving oxygen mass transfer in the treatment of gold ores were achieved with the use of Degussa's peroxide-assisted leach or PAL (Loroesch *et al.*, 1988) and Kamyr's carbon-in-leach-with-oxygen process (CILO) (Elmore *et al.*, 1988). The contributions related to the use of oxygen in cyanidation have been reported by Revy *et al.* (1991), Kondos *et al.* (1995) and Liu and Yen (1995).

Efforts have also been invested in the development of an efficient device that could enhance oxygen dispersion (Jara and Harris 1994; Sceresini, 1997; McLaughlin *et al.*, 1999). The practice of continuous oxygen monitoring and control stabilizes process performance and compensates for disturbances related to changes in oxygen requirements. Improvements in the design of oxygen probes have added further robustness to the leaching operation and control strategy. The probe used at East-Malartic/Bousquet operation has proven to be reliable with a high operating availability and minimum maintenance, owing to the ease of its calibration routine (McMullen and Thompson, 1989).

The FILBLAST Gas-Shear Reactor has been used to improve gas mass transfer efficiency. The proponents of this technology claim that it improves dissolved oxygen concentration, reduces oxygen consumption, and improves the gold-leaching rate and recovery. The technology has been tested at the industrial scale (Sceresini, 1997). Column-flotation spargers and high-efficiency mixers are alternatives worth considering. Inverted-cone diffusers under the mixing propeller are also frequently used.

3.3. Lead nitrate

Three methods are used to adjust the rate of addition of lead nitrate. The first method is the *Prussian blue test*, which is used at Doyon Mine (Deschênes and Putz, 1999). This approach has proven to be unreliable. The second method involves the determination of the reducing power of a pre-leach solution, and was used at Lupin Mine to determine the efficiency of the pre-aeration circuit (Fulcher and Kim, 1987). This method determines the concentration of thiosulfate in solution. The last and the most common method is based on the gold content of the leach residue. The addition rate of lead nitrate is adjusted according to the gold content of the leach residue. Significant cyanide and oxygen demands are also considered to be indicators in the adjustment of lead nitrate addition. These strategies rely on fluctuations in the circuit. As the knowledge base evolved, it became clear that the control strategy for lead nitrate addition was reactive rather than proactive.

The role of lead nitrate (or lead salts) is:

- To decrease the dissolution of metallic sulfides by forming a coating, which consequently reduces (a) the dissolution of sulfide minerals; (b) the consumption of oxygen by sulfides; and (c) the cyanide consumption.
- To enhance the dissolution of gold by (a) decreasing the importance of the passive layer formed on gold grains; (b) forming a precipitate on gold grains to create a corrosion pile which makes gold anodic and more inclined to dissolve; and (c) depolarizing the reduction of oxygen.

Applying a pretreatment prior to cyanidation can significantly reduce the dissolution of sulfide minerals. This, in turn, will improve the performance of cyanidation. Pre-aeration or pre-leaching is used for ores containing reactive sulfide minerals such as pyrrhotite, marcasite and high concentrations of pyrite. When a pretreatment is required, lead nitrate is often added at this step. The pretreatment used at Geant Dormant Mine is a good example of this application (Deschênes and Fulton, 2002).

Lead nitrate addition has an effect on leaching kinetics and overall extraction, as illustrated in Fig. 8 (Deschênes, 2004). Overall, gold extraction increased by 6%, from 79.2%, with no lead nitrate, to 85.2% with 500 g/t

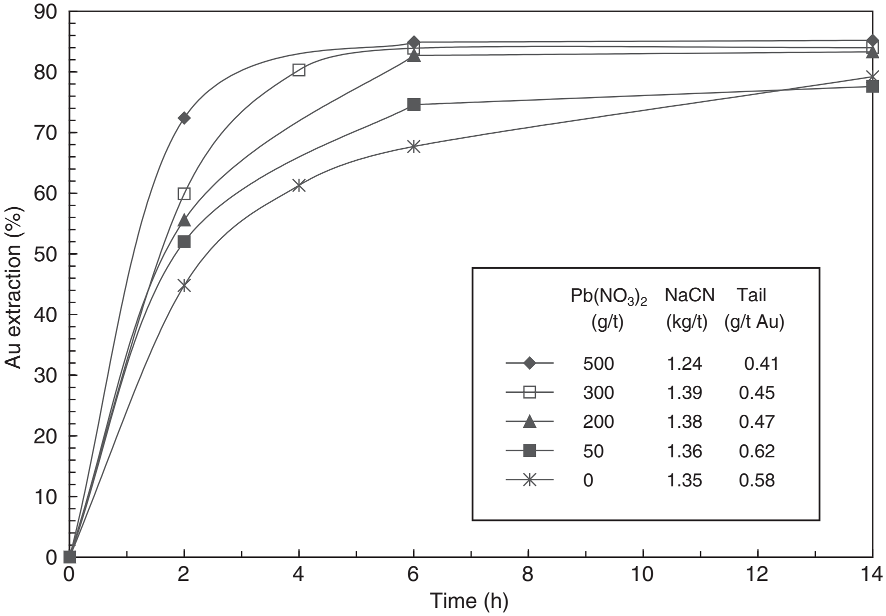

Fig. 8. Effect of lead nitrate addition on the gold-leaching kinetics of a sulfide-bearing gold ore (Deschênes, 2004).

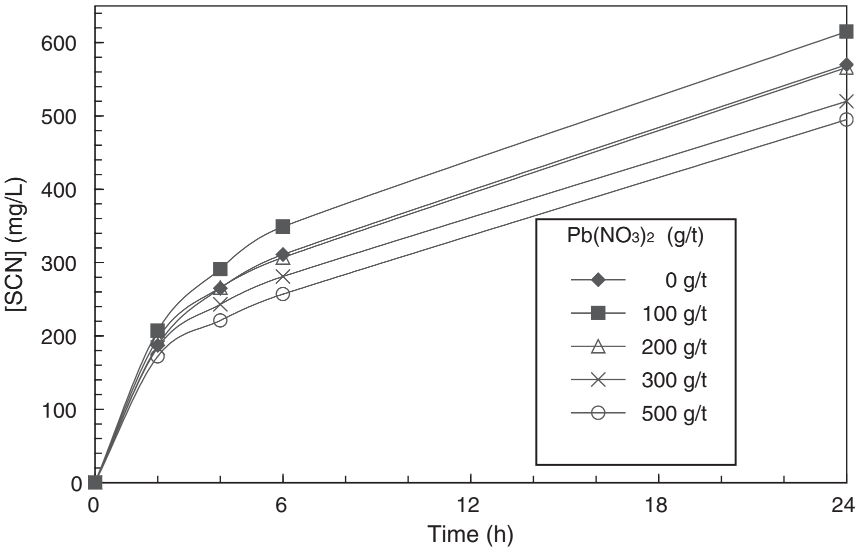

Fig. 9. Effect of lead nitrate addition on the formation of thiocyanate for the leaching of a sulfide-bearing gold ore (Deschênes, 2004).

lead nitrate. Cyanide consumptions were 1.35 kg/t without lead addition, and 1.24 kg/t for 500 g/t lead nitrate addition, a reduction of only 8%.

A relationship was established with the formation of thiocyanate (Fig. 9). The reaction rate of free cyanide with thiosulfate and other sulfur species to form thiocyanate decreased gradually with the increase in lead nitrate addition for concentrations of 100 to 500 g/t. This relationship is used to determine a targeted concentration of thiocyanate in the slurry.

4. APPLICATIONS

4.1. Low-sulfide ore

Even a very low sulfide concentration could have a significantly detrimental impact on gold-leaching kinetics and overall gold extraction. Cyanidation at Fort Knox Mine was seriously affected by a minor concentration of metallic sulfide. The economic consequences were very important. Fort Knox cyanidation plant processes 38,000 tpd of a low-grade (1.0 g/t Au), free-milling gold ore with a low metallic sulfide component (below 0.3%), by gravity (11% recovery) and by cyanidation (89% recovery). The short retention time (20 h), low temperature (7°C) and low grade make leaching kinetics critical for the performance of the process. A new ore, which represented only 14.4% of the mill throughput (and contains slightly more sulfide minerals in the form of pyrite, arsenopyrite and stibnite), resulted in a gold extraction decreasing from 87 to 72.6% (Hollow *et al.*, 2003). No leaching kinetics problem was identified in the laboratory investigations on the new ore fed into the circuit. The decrease in gold extraction only occurred on leaching the blend. After 12 months of laboratory investigation, three options were identified to solve the problem: leaching at pH lower than 10, increasing the DO of the slurry, or using lead nitrate. The significant effect of pH on gold-leaching pointed to stibnite as the origin of the problem.

Lead nitrate addition was selected as the most effective approach, both technically and economically. The use of a low pH was not an option in the Fort Knox mill, where operating the circuit at a reduced pH resulted in above-threshold-level HCN concentrations in the tank enclosures. The enclosures must enable the circuit to be operated and maintained in a sub-arctic environment. Extra equipment was needed to increase the DO in the leaching slurry. The antimony content of the feed was monitored against the performance of the plant with and without addition of lead nitrate (Fig. 10). An improvement of about 5% gold extraction was observed at low concentrations of antimony.

The improvement in leaching kinetics is illustrated in Fig. 11 (laboratory experiment). The leaching rates of the two systems were similar in the first 5 h. In the case of the system without lead nitrate, the gradual dissolution of

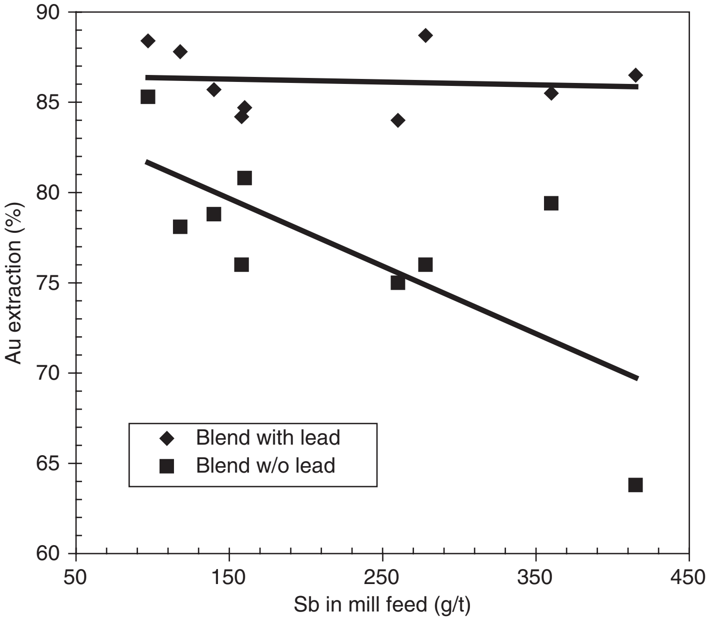

Fig. 10. Effect of antimony concentration in the feed on the cyanidation of blended mill feed composites with and without lead nitrate (Hollow *et al.*, 2003).

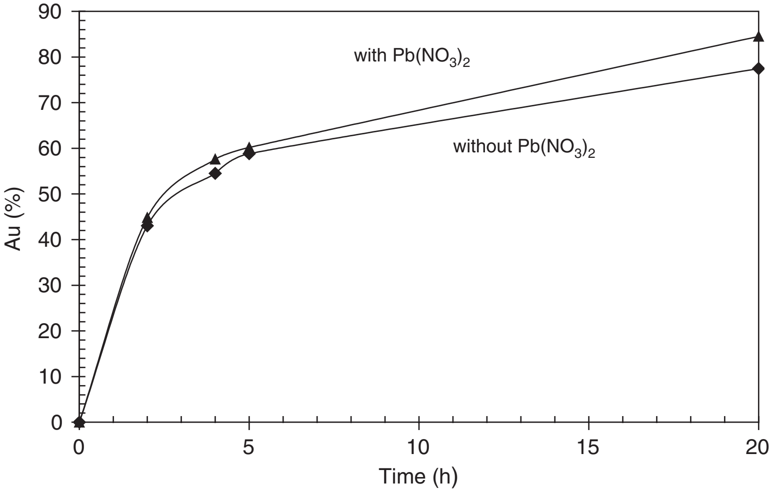

Fig. 11. Improvement of gold-leaching rate of Fort Knox feed composites with and without lead nitrate (Hollow *et al.*, 2003).

stibnite decreased the gold-leaching kinetics after the 5-h point. The gold extraction gap between the two systems increased with time.

Plant data indicated that the addition of lead nitrate increased gold extraction from 87 to 91.7% and, for the 18 months evaluated, resulted in gold production in excess of 49,000 oz higher than that estimated for the non-lead nitrate reagent scheme.

4.2. Gold ore with pyrite and arsenopyrite

The New Britannia Mine project on improving of gold-leaching comprised three steps: (1) laboratory testwork to establish the leaching parameters, leaching kinetics and reagent consumptions; (2) modification of the leaching strategy at the plant scale; and (3) implementation of an automated control of cyanide addition (Healy *et al.*, 2000). The cyanide control system was developed by Degussa Huels, who also supplied the online cyanide analyser (potentiometric titration). The ore was mostly free-milling gold (90%) at a grade of 4.35 g/t, with 2.5–3.0% pyrite, 3.0% arsenopyrite and a P90 of 74 µm. Initial plant throughput and retention time were 2155 t/d and 50 h, respectively. Laboratory results (Fig. 12) indicated a significant improvement in gold-leaching kinetics and overall gold extraction with the addition of lead nitrate before leaching. The faster leaching kinetics allowed a 14% increase in throughput. Overall, modifications to the circuit contributed to a 4% increase in gold recovery and a 27% reduction in operating costs. The 21%

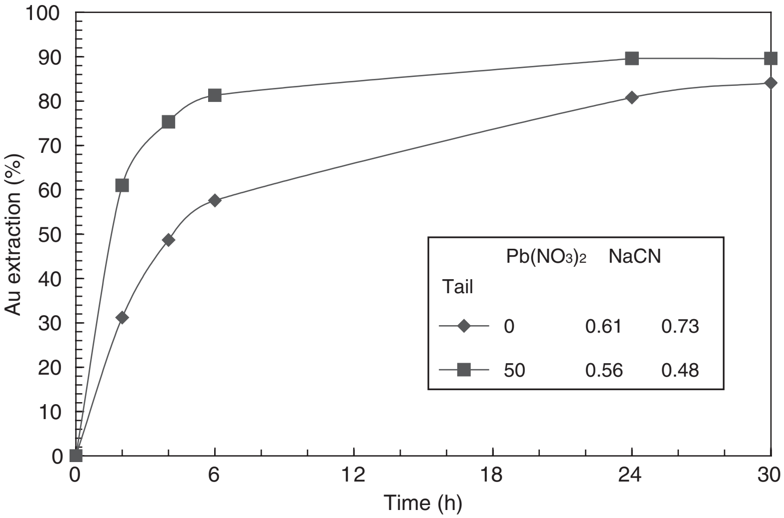

Fig. 12. Gold-leaching kinetics of New Britannia Mine ore (Healey *et al.*, 2000).

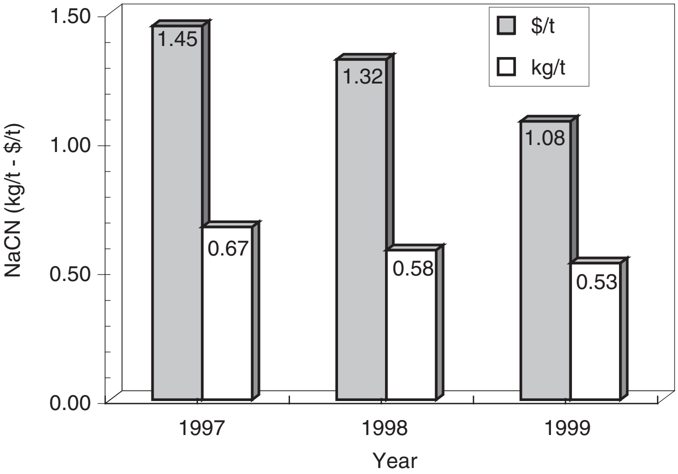

Fig. 13. Cyanide consumption of New Britannia Mine during plant improvements (Healey *et al.*, 2000).

reduction in cyanide consumption resulted in the shutdown of the cyanide destruction plant. Fig. 13 illustrates the reductions in cyanide consumption and annual costs. These improvements represented an additional gross annual revenue (CAD) of $1.9 million.

4.3. Gold ore with pyrrhotite

The Musselwhite Mine treats a pyrrhotite-bearing ore containing mostly free gold (5.5–5.8 g/t Au, 4.2% pyrrhotite). The pyrrhotite is both monoclinic (50%) and hexagonal (50%). Cyanidation with the addition of lead nitrate was already part of the plant strategy at the beginning of the project. Fig. 14 illustrates cyanidation experiments conducted to demonstrate gold-leaching kinetics when lead nitrate is added during cyanidation (Deschênes *et al.*, 2002b). The absence of lead nitrate is associated with a 12.1% reduction in gold extraction for the retention time of the leach circuit. Laboratory work indicated an increase in gold-leaching kinetics with a higher dissolved-oxygen content, but such a system is not as effective as a leach with lead nitrate.

The introduction of oxygen and an online cyanide analyser enhanced leaching kinetics and resulted in a 0.61% increase in gold recovery, from 95.20% in 1999 to 95.81% in 2000. Benefits of the use of oxygen were more pronounced in the hot summer months when higher slurry temperatures depleted dissolved oxygen content and pyrrhotite was more reactive. Cone spargers were installed to make oxygen use more efficient. A 2.0% improvement in gold recovery was obtained (July 2000 vs. July 1999) for an additional gross revenue (CAD) of $0.5 million. Cyanide consumption decreased by approximately 8%. However, without lead nitrate, oxygen cannot be used to process this sulfide-bearing gold ore. The passive layer formed on gold

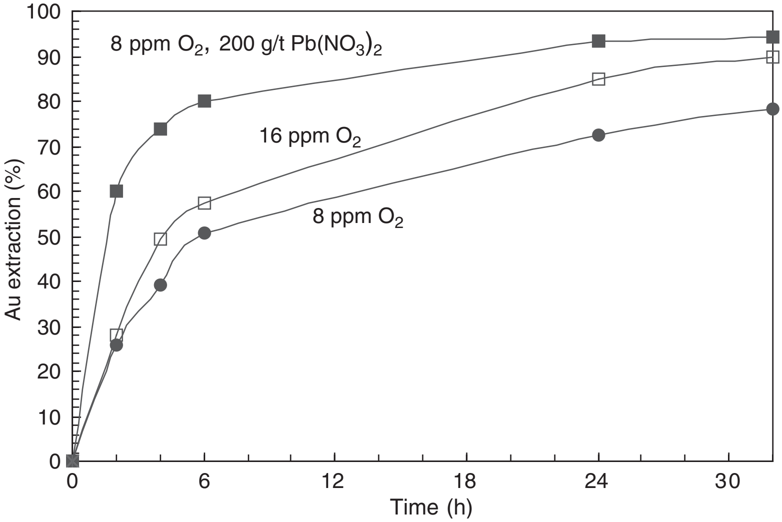

Fig. 14. Effect of lead nitrate and oxygen addition on the leaching of a pyrrhotite-bearing gold ore with addition of lead nitrate (pre-leaching: pH 11.2, 0.5 h, 8 ppm O_2; cyanidation: pH 11.2, 380 mg/L NaCN, 8 ppm O_2 – after Deschênes *et al.*, 2002b).

grains by the dissolution of pyrrhotite cannot be avoided with oxygen as it was with lead nitrate.

5. CONCLUSIONS

Both implementation of instrumentation for chemical monitoring and development of metallurgical reagent-addition strategies have contributed to improve the performance of cyanidation in terms of higher gold extraction and lower addition of reagents. Adequate control of oxygen and lead nitrate has proven beneficial in the optimization of leaching kinetics. This is particularly critical for increased production throughput while maintaining performance. Significant paybacks on improved gold-leaching with cyanide have been obtained.

Surface analysis studies of the passive coatings formed on gold during leaching contribute to a better understanding of the mechanisms involved in gold dissolution. The findings thus far indicate that these mechanisms are complex and involve electrochemical reactions as well as mass transfer and chemical reactions. These fundamental studies complement applied research and enhance the understanding of the phenomena.

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Chapter 21

Alternative lixiviants to cyanide for leaching gold ores

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Over 25 alternative lixiviant processes to cyanide have been tested in the laboratory, some of which have been successful for niche applications. The process conditions, applications and current status of the most attractive are reviewed in this chapter, with an emphasis on publications since 1995. Most of the work has focussed on thiosulfate, thiourea and halide-leaching systems. Pressure-oxidative chloride-, sulfide- and ammonia-leaching processes are generally more applicable for the extraction of gold or platinum group metals as a by-product from base metal sulfide concentrates. Despite the research interest and pilot-plant trials on many non-cyanide gold lixiviants, a viable alternative gold process is still at the early developmental stage. The most advanced is the thiosulfate heap leaching of low-grade carbonaceous *preg-robbing* ores by Newmont Mining. In most alternative cyanide-leaching processes, reductions in the quantity of reagents used, reagent consumptions and improvements in recovery technology are required. Some chemicals used, such as ammonia, also pose health, safety and environmental concerns. Consequently, proper disposal of wastes and sustainable development issues will have to be addressed by mining companies.

1. INTRODUCTION

The major impetus in seeking alternative lixiviants to cyanide arises from the environmental hazards posed by cyanide's toxicity, with numerous environmental groups throughout the world actively pursuing a ban on its use.

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Table 1
Alternative lixiviants to cyanide (% of publications)

(1) Thiosulfate ($Cu(II)–NH_3–S_2O_3$)	33	(6) Ammonia/O_2 or Cu(II)	2
(2) Thiourea (Fe(III), $CS(NH_2)_2$)	26	(7) Bacteria/natural acids	3
(3) Halide (Cl_2, Br_2, I_2)	15	(8) Thiocyanate/Fe(III)	4
(4) Oxidative chloride processes	4	(9) Nitriles/O_2 or Cu(II)	3
Aqua regia		(10) Cyanide + other combination	5
Acid ferric chloride		Ammonia-cyanide	
Haber process		Alkali cyanoform	
(5) Sulfide systems	5	Calcium cyanamide	
Sodium sulfide		Bromo-cyanide	
Polysulfide		(11) Others	2
Biocatalysed *bi*sulfate		Electrolysis of ore slurry	
*Bi*sulfide/sulfur dioxide		CSUT	
N-catalysed pressure process		DMSO, DMF	
		BioD leachant	

Approval for any new gold project using cyanide is extremely unlikely in some areas around the world. Elsewhere, increasing regulatory scrutiny of new gold projects and a lowering of acceptable levels of cyanide discharge are of considerable concern to mining companies.

Over the past two decades, a significant amount of literature has examined alternative extraction processes to cyanide for recovering gold from different ores. The chemistry of these alternative processes has been reviewed by Avraamides (1982), Nicol *et al.* (1987), Hiskey and Atluri (1988), and more recently by Sparrow and Woodcock (1995). Overall there are over 500 references that appear related to the application of alternative lixiviants to cyanide for leaching gold. In addition, there has been work carried out by private companies, research institutions and commercial metallurgical laboratories that is not readily accessible. Altogether, 27 possible solvents have been investigated as alternatives to cyanide for leaching gold. These can be grouped into 11 categories as outlined in Table 1 that also shows the percentage of papers and patents published for each of the different lixiviants.

Three quarters of the work has focussed on thiosulfate, thiourea and halide leach systems. The oxidative chloride-, sulfide- and ammonia-leaching processes have generally been used for extraction of a wide range of elements (*e.g.*, base metals, PGMs), with gold as a by-product. Thiocyanate, nitriles and combined cyanide lixiviant systems contain cyanide or derivatives of it, and therefore may not be considered by some to be different to cyanide. Most of the other lixiviants discussed by Sparrow and Woodcock (1995) are of academic interest or have received limited publication. Therefore, this section will be concerned with the first eight categories and will concentrate on most recent literature.

1.1. Stability of alternative lixiviants and gold complexes

Despite the research interest in non-cyanide gold lixiviants, alternative gold processes are still at the early developmental stages. A key factor affecting ultimate commercial success is the stability of the lixiviant and the gold complex in solution. In some cases, there is a limited understanding of solution and pulp chemistry. This is partly associated with (i) the difficulties in measuring reliable equilibrium data for various gold(I/III) complexes, (ii) the lack of knowledge on mixed-ligand complexes and (iii) different kinetic stabilities of gold(I) complexes with respect to disproportionation (Senanayake, 2004).

The equilibrium data for complex formation, dissolution, precipitation, hydrolysis and disproportionation reactions of gold(I/III) compounds for a range of non-cyanide ligands has been recently re-evaluated (Senanayake, 2004). The stability constants (β_2 or β_4) for various gold(I) and (III) complexes, together with their standard reduction potentials, are shown in Table 2. Clearly the cyanide complex is more stable than any of the other reagents with thiosulfate, thiourea and bisulfide several orders of magnitude less. While the stability constant for the gold ammonia complex has been reported to be around 26.5, recent unpublished data indicate a value of around 13.

As a result of the wide range of values for the stability constants of the gold complexes, the standard reduction potentials for the different gold ligand species vary by almost 2 V (Ritchie *et al.*, 2001). For many of the ligands,

Table 2
Stability constants and standard reduction potentials for gold complexes at 25°C

Ligand	Au(I) or Au(III) Complex	log β_2 or β_4	E° Au(I or III)/Au (V vs *S*HE[a])	pH range
CN^-	$Au(CN)_2^-$	38.3	−0.57	>9
$S_2O_3^{2-}$	$Au(S_2O_3)_2^{3-}$	28.7	0.17	8–10
$CS(NH_2)_2$	$Au(NH_2CSNH_2)_2^+$	23.3	0.38	<3
Cl^-	$AuCl_2^-$	9.1	1.11	<3
	$AuCl_4^-$	25.3	1.00	
Br^-	$AuBr_2^-$	12.0	0.98	5–8
	$AuBr_4^-$	32.8	0.97	
I^-	AuI_2^-	18.6	0.58	5–9
	AuI_4^-	47.7	0.69	
HS^-	$Au(HS)_2^-$	29.9	−0.25	<9
NH_3	$Au(NH_3)_2^+$	26.5(13)	0.57	>9
Glycinate	$Au(NH_2CH_2COO)_2^-$	18.0	0.632	9
SCN^-	$Au(SCN)_2^-$	17.1	0.66	<3
	$Au(SCN)_4^-$	43.9	0.66	
SO_3^{2-}	$Au(SO_3)_2^{3-}$	15.4	0.77	>4

Note: It is believed that the value in parentheses may be the true stability constant for gold(I) diammine.
[a] Standard hydrogen electrode.

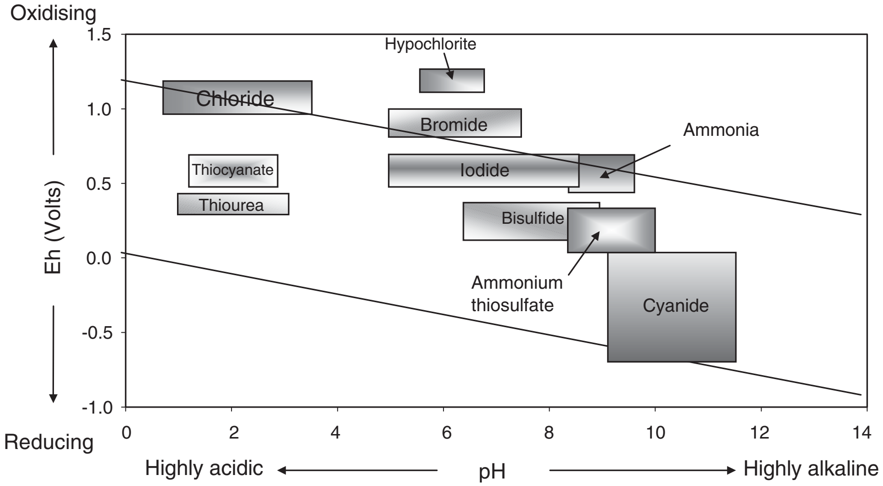

Fig. 1. Eh–pH diagram showing typical operating regions for gold lixiviants.

such as thiosulfate, oxidation of the ligand occurs at a potential below that of the corresponding Au(I) complex while the reverse is true for ligands SCN^- and Cl^-. Therefore, there is a competing reaction to gold dissolution with most alternative lixiviants, which increases reagent consumption. The presence of Fe(III) catalyst in acid thiourea solutions and Cu(II) catalyst in alkaline thiosulfate solutions also results in rapid oxidation of the ligand. Oxygen itself is often a poor oxidant due to low rates of mass transport and slow rates of reduction on gold surfaces in non-cyanide systems. With the exception of the halides, the alternative lixiviants are clearly more complex to operate than cyanide.

Most reagents have a small operating window where the alternative lixiviants effectively dissolve gold compared with cyanide (Fig. 1). The high oxidizing potentials involved with some lixiviants inevitably lead to high reagent consumptions due to reaction with any sulfide minerals as well as oxidation of the reagent itself (Nicol, 1980). This applies particularly to thiocyanate and thiosulfate. Consequently, leaching conditions have to be better controlled than those used for cyanide leaching. Equally important, although not always considered, is the adsorption of reagents or/and precipitation of gold onto some clay and gangue minerals, which will be detrimental to overall gold recovery.

2. THIOSULFATE LEACHING

In recent years, thiosulfate has been considered the most attractive alternative to cyanide for leaching gold, with many investigations taking place around the world. This is primarily based on its low toxicity and its potential use on preg-robbing carbonaceous ores that cannot be readily treated by conventional cyanidation (see Chapter 38). The ammoniacal thiosulfate-leaching process for gold and silver extraction has been recently reviewed in terms of the leaching mechanism, thermodynamics, thiosulfate stability and gold recovery options (Aylmore and Muir, 2001; Muir and Aylmore, 2004; Molleman and Dreisinger, 2002; Grosse *et al.*, 2003). Recent advances in understanding the thiosulfate process are presented in the following chapter (Chapter 22; Muir and Aylmore, 2004) and therefore this process is only mentioned briefly here for clarification.

2.1. Thiosulfate – process conditions

The chemistry of the ammonia–thiosulfate–copper system is relatively complicated. However, by maintaining suitable Eh and pH conditions and by controlling the concentrations of thiosulfate, ammonia, copper and oxygen in the leach solution, high gold extractions can be achieved with low reagent consumption for some ores (Wan, 1997).

The oxidation of metallic gold to aurous Au(I) ion in ammoniacal thiosulfate is catalysed by the presence of copper(II) as follows:

$$\mathrm{Au} + 5\mathrm{S_2O_3^{2-}} + \mathrm{Cu(NH_3)_4^{2+}} \rightarrow \mathrm{Au(S_2O_3)_2^{3-}} + 4\mathrm{NH_3} + \mathrm{Cu(S_2O_3)_3^{5-}} \tag{1}$$

The redox equilibrium between the cuprous–cupric couple in ammoniacal thiosulfate solution is represented by the following reaction (Wan, 1997) with oxygen regenerating Cu(II):

$$2\mathrm{Cu(S_2O_3)_3^{5-}} + 8\mathrm{NH_3} + \tfrac{1}{2}\mathrm{O_2} + \mathrm{H_2O} = 2\mathrm{Cu(NH_3)_4^{2+}} + 2\mathrm{OH^-} + 6\mathrm{S_2O_3^{2-}} \tag{2}$$

In addition, oxidative decomposition reactions of thiosulfate occur, which result in the formation of polythionates such as *tetra*thionate and *tri*thionate. The form and quantity of these degradation products are dependent on reagent concentrations, dissolved oxygen concentrations, pH, Eh and temperature.

2.2. Thiosulfate – optimum conditions for leaching

Optimum conditions for leaching appear to vary depending upon the mineralogy of the ore treated and the deportment of gold. Preferred conditions reported by Muir and Aylmore (2004) for treating oxidized ore are 0.050 M thiosulfate (6.6 g/L), 0.40 M total ammonia (6.8 g/L) and 60 mg/L Cu(II) at pH 9.5 and 40°C. The Eh is maintained around 0.3 V by addition of air to give DO levels between 1 and 3 mg/L. Under the preferred leach conditions, thiosulfate consumption was found to range from 2 to 5 kg/t ore, representing ~30% loss over an 8-h period. Ammonia losses were ~1 kg/t at 25°C, but it appears that most was absorbed on the ore itself.

For heap leaching carbonaceous ores, a leach solution containing 0.1–0.2 M $(NH_4)_2S_2O_3$, at least 0.1 M NH_3 and up to 60 mg/L of Cu(II) has been found suitable (Wan *et al.*, 1994). Thiosulfate consumption was generally around 3–5 kg/t ore. Similar reagent concentrations were used by Lakefield Research at 40–60°C and pH 8.0 to leach Barrick Gold carbonaceous refractory ores after pressure-oxidation pre-treatment (Fleming *et al.*, 2003). Up to 95% of the gold was extracted from the finely divided gold left in the oxidized residue.

3. THIOUREA LEACHING

Interest in the thiourea process for leaching gold occurred mainly during the 1980s and early 1990s. This earlier work was reviewed by Groenewald (1977), Hiskey (1981, 1988) and Lan *et al.* (1993). Considerable research has been carried out by Canmet and Mintek for gold extraction in underground (Tremblay *et al.*, 1996) and *in-stope* applications (*e.g.*, van Staden and Laxen, 1989). In addition, Newmont Mining and Barrick Gold looked closely at thiourea leaching as a potential process for treating refractory ores. In recent years, interest in this leaching approach has decreased due to the potential carcinogenic properties of thiourea (personal communication). However, there is still laboratory research being carried out in Eastern Europe (*e.g.*, Gönen, 2003; Örgül and Atalay, 2000, 2002). Also, a novel leaching process was recently patented by Dublin University in Ireland (Kavanagh *et al.*, 2000). Some recent work on the oxidation of gold and thiourea in acidic thiourea solution has been carried out by Zhang *et al.* (2001) and Li and Miller (2002). A number of papers have also been published by a group of researchers in China on the dissolution of gold electrodes in an alkaline thiourea system (*e.g.*, Chai *et al.*, 1999). However, thiourea is generally unstable in alkaline media and its application to ores has not been demonstrated.

3.1. Thiourea – process conditions

In practice, thiourea leaching of gold is typically performed at thiourea concentrations of 0.13 M (10 g/L), ferric ion concentrations of 0.09 M (5 g/L), pH values of 1–3 and at potentials between 0.4 and 0.45 V (vs. SHE). The overall reaction that describes gold dissolution in thiourea and ferric ion solutions is

$$Au + 2NH_2CSNH_2 + Fe^{3+} = [Au(NH_2CSNH_2)_2]^+ + Fe^{2+} \tag{3}$$

Various oxidants, including ferric ion, hydrogen peroxide, manganese dioxide, *mono-per*-oxysulfate compounds and ozone have been examined, but ferric ion is the most common (Sparrow and Woodcock, 1995). The gold-leaching reaction is very sensitive to pH and the redox potential (Kenna and Moritz, 1991). Furthermore, thiourea is intrinsically unstable and decomposes rapidly to substances that are unable to leach gold. Tremblay *et al.* (1996) concluded that to limit the thiourea decomposition and optimize gold extraction, it was necessary to maintain the leaching potential between 0.42 and 0.45 V (vs. SHE). Thus, careful control of solution potential in a commercial process is necessary.

Leaching rates as high as 10 times faster than for cyanide have been reported, with silver and gold reacting differently, implying that the dissolution mechanisms are not the same. Gold in contact with pyrite or chalcopyrite also exhibits an enhanced gold dissolution rate (van Deventer *et al.*, 1990). However, thiourea also forms strong complexes with some base metals such as copper and to a lesser extent lead and zinc (Deschenes *et al.*, 1994; Fang and Muhammed, 1992; Alodan and Smyrl, 1998), which can increase thiourea consumption.

High potentials during leaching produce an oxidative degradation of thiourea that proceeds via formamidine disulfide ($NH_2(NH)CSSC(NH)NH_2$), which eventually decomposes to thiourea ($CS(NH_2)_2$), cyanamide (NH_2CN) and elemental sulfur (S^0). Acid hydrolysis also forms urea (NH_2CONH_2) and hydrogen sulfide (H_2S) as follows:

$$2NH_2CSNH_2 + 2Fe^{3+} = NH_2(NH)CSSC(NH)NH_2 + 2\,H^+ + 2Fe^{2+} \tag{4}$$

$$NH_2(NH)CSSC(NH)NH_2 = NH_2CSNH_2 + NH_2CN + S^0 \tag{5}$$

$$NH_2CSNH_2 + H_2O = NH_2CONH_2 + H_2S \tag{6}$$

Elemental sulfur and hydrogen sulfide are undesirable species during gold leaching. It is believed that both these species cause a decrease in the leaching rate due to surface passivation, and hydrogen sulfide may cause re-precipitation of the gold (Sparrow and Woodcock, 1995; Munoz and Miller, 2000).

For optimum leaching, the oxidant must be added at such levels as to oxidize ~50% of the thiourea to formamidine disulfide. Gold dissolution can be accelerated effectively by the presence of formamidine disulfide or by using a higher temperature (Zhang *et al.*, 2001). However, excess oxidant will increase thiourea consumption significantly. In practice, it is necessary to use a stabilizer to convert formamidine disulfide back to thiourea, or to complex the oxidant.

3.2. Thiourea – stabilizers

To combat the loss of thiourea, several workers have used additions of sulfur dioxide or substantial quantities of sulfite and iron(III) complexing acids with mixed success (see Sparrow and Woodcock, 1995 and papers therein). Deng *et al.* (2001, 2002) reported on testwork involving the thiourea leaching of a bio-oxidized primary gold sulfide ore to which 4.5 g/L Na_2SO_3 had been added. The consumption of thiourea decreased significantly from 12 to 3 kg/t and extraction time was shortened from 6 to 1 h at a pH value of 2. Thiourea-substituted compounds such as *N,N′*-ethylene-thiourea (Schulze, 1985) are more stable to oxidation and minimizes reagent consumption (Kenna and Moritz, 1991). Kenna (1991) patented a thiourea gold extraction method in which *di*- and *tri*-carboxylic acids, fluorides, fluosilicic acid and fluosilicate salt, EDTA (ethylene *di*amine *tetra*acetic acid) and EDTA salts are used to complex the ferric ion to reduce thiourea consumption. Cysteine ($HSCH_2CH(NH_2)COOH$) has also been found to be an effective reagent for the stabilization of thiourea (Ardiwilaga, 1999). However, cysteine prevented the formation of formamidine *di*sulfide, which is required to maintain a high gold-leaching rate and consequently gold recovery was reduced.

Washing with water and with varying concentrations of sulfuric acid prior to thiourea leaching has been found to be advantageous by several workers (*e.g.*, Kavanagh *et al.*, 1994; Tremblay *et al.*, 1996; Lacoste-Bouchet *et al.*, 1998; Deng *et al.*, 2001). The value of this approach varied from ore to ore; however, pre-treatment with acid has been shown to not only remove easily leachable metals, but to allow the thiourea system to stabilize more quickly and to prevent unnecessary reagent consumption due to the precipitation of base metals. Activated carbon, some clay and gangue minerals adsorb thiourea and its gold complex, thus reducing the overall gold recovery (Zhang, 1995).

3.3. Thiourea – applications

Applications of thiourea leaching have been demonstrated on the laboratory scale after fine grinding (Kusnierova *et al.*, 1993), mechano-chemical milling (Balaz *et al.*, 2003), bacterial oxidation (Caldeira and Ciminelli, 1993; Wan *et al.*, 1995; Deng *et al.*, 2001; Deng and Liao, 2002), after pressure oxidation (Yen and Wyslouzil, 1985; Bruckard *et al.*, 1993; Murthy *et al.*, 2003) and after roasting (Bilston *et al.*, 1990; Moussoulos *et al.*, 1984). The perceived advantage is that the acidic pre-oxidized sulfide ore can be directly leached with thiourea without a neutralization step that would be required for leaching with cyanide. Thiourea has also been applied to oxide ores with mixed results (Ubaldini *et al.*, 1998, McNulty, 2001).

Most successful applications have been carried out on ores that have a high content of *cyanicides* such as antimony, or sulfide ores that have undergone bacteria oxidation or pressure leaching. A small-scale industrial application of a gold–antimony concentrate was demonstrated at the New England Antimony Mine in Australia in the early 1980s, with gold recovery on activated carbon (Hisshion and Waller, 1984). Thiourea concentrations have ranged from 2 to 15 g/L, acid from 1 to 150 g/L (or higher), pH 1–3 in laboratory and pilot-scale testwork. The oxidant has varied from 0 to 20 g/L, where in some cases the iron from the ore has been used. Interestingly, gold extraction has not always been as high as that obtained using cyanide.

In general, reagent consumption is dependent on reagent concentration, and values reported in the literature seem to be considerably higher (thiourea consumptions ranging from 4 to 47 kg/t) than those for cyanide, thus resulting in higher extraction costs. The high consumption of thiourea, acid (for pH control), peroxide and sulfur dioxide (for Eh control) make the overall cost of the process between 1.5 and 2 times the cost of cyanidation for the same material.

A 450 t pilot-test heap leach, using acidic thiourea, was conducted by Newmont at the Carlin mine after bio-oxidation (Wan *et al.*, 1995). The bio-oxidation test heap was washed with fresh water following bio-oxidation and drained before thiourea leaching. The thiourea solution at a concentration of 10 g/L was pumped onto the heap at a flow rate of 30–45 L/min with the whole operation running over a 110-day period at a pH value below 2.5. The redox potential was generally in the range of 0.43–0.5 V (vs. SHE). No chemical control was required during the thiourea leach in terms of pH or Eh adjustments. Outcomes of this work were that thiourea yielded poor gold extraction kinetics because of the large particle size used and the cold temperature experienced during the pilot run. A maximum of 29% of the gold was recovered. Gold recovery from the pregnant solution using activated carbon or cation-exchange resin was ineffective. Continuous recirculation of the solution caused elemental sulfur to form, which coated the carbon and resin, impeding the recovery process.

3.4. Thiourea – current status

With thiourea labelled as a potential carcinogen, it is difficult to see it providing a replacement for cyanide in the near future. Extensive investigations on all aspects of leaching have been evaluated and while there would be some potential niche applications, it appears that the sensitivity of leaching conditions would not make it an obvious choice compared with other alternatives. Lower thiourea concentrations would be required to make it economic. Recovery of gold from thiourea solution also requires further development.

4. HALIDE LEACHING

Chlorine, bromine and iodine are well-known lixiviants for leaching gold, as recently reviewed by Tran *et al.* (2001). Chlorination was applied extensively in the late 19th century before the introduction of the cyanidation process. Bromine/bromide for leaching gold from ores was reported as early as 1846. Chlorination was used extensively for pretreating refractory and carbonaceous ores in several plants in the USA in the 1980s (Marsden and House, 1992). Renewed interest in halides as a lixiviant for leaching gold occurred in the 1990s after several patents based on the bromine/bromide systems were lodged (see Pesic *et al.*, 1992 and references therein; Tran *et al.*, 2001).

For completely oxidized materials, the chloride-based leaching processes have a clear advantage in applications where a high dissolution rate is required. The use of chlorine is a proven technology in gold-refining and electroplating processes, as discussed in Chapters 27 and 36. Most notable in recent years has been the development of the Minataur$^{\text{TM}}$ process by Mintek (Feather *et al.*, 1997). However, halogens have proved to be very reactive with other ore minerals, especially sulfides. Under typical halide-leaching conditions, reagent consumptions would be very high if the ore contained significant sulfide minerals.

4.1. Halides – process conditions

Typical conditions used for leaching gold by halogens are listed in Table 3.

In all halogen processes, high-oxidation conditions are required. The general equation describing the reaction of gold with chlorine or bromine is as follows:

$$2\text{Au} + 3\text{X}_2 + 2\text{X}^- = 2\text{AuX}_4^- \quad \text{where X} = \text{Cl, Br} \tag{7}$$

The complex AuCl_2^- is formed initially and is rapidly oxidized to AuCl_4^- (Nesbitt *et al.*, 1990; Sun and Yen, 1992). In the iodine system, iodine reacts with iodide in aqueous solution to form I_3^- ions with Au(I) rather than forming the Au(III) complex (E° for $\text{AuI}_2^- < \text{AuI}_4^-$; Tran *et al.*, 2001). The Au(III) complex is not stable because this ion oxidizes iodide ion to iodine and the Au(III) complex is reduced to Au(I) complex:

$$2\text{Au} + \text{I}_3^- + \text{I}^- = 2\text{AuI}_2^- \tag{8}$$

Unlike gold cyanide, which is very stable and does not decompose easily in most applications, the stability of gold halide is dependent on the solution pH,

Table 3
Typical conditions used in leaching gold with halides

Reagent	Ligand	Oxidant	Gold complex	Typical leaching conditions	pH
Chlorine	Cl^-	Cl_2 or HClO	AuCl_4^-	5–10 g/L Cl_2 5–10 g/L NaCl	<3
Bromine	Br^-	Br_2	AuBr_4^-	2–5 g/L Br_2, 0–10 g/L NaBr	5–8
Iodine	I^-	I_2	AuI_2^-	1 g/L I_2, 9 g/L NaI	5–9

composition (with respect to halide concentration), solution potential and the presence of reductants (such as metals and sulfidic minerals) in the ores. A residual amount of oxidant is required to maintain a high solution potential to avoid the precipitation of metallic gold from solution (Tran *et al.*, 2001).

The gold dissolution rate can be very high and is dependent on solution pH, lixiviant and oxidant concentrations (Sergent *et al.*, 1992; Tran *et al.*, 2001). Overall, the stability of halides is in the order of $I > Br > Cl$, whereas the rate of reaction is $Cl > Br > I$.

4.1.1. *Chlorine*

The fundamental electrochemical kinetics of gold dissolution in chloride media, and the chemistry of the chlorine process, have been described by Finkelstein (1972), Nicol (1976) and Avraamides (1982). The dissolution of gold in chloride media was evaluated by Yen *et al.* (1990) and Tran *et al.* (1992), using hypochlorite as an oxidant. The weight loss of gold strips immersed in different chloride–hypochlorite mixtures (up to $20\,mg/cm^2\,h$) was much faster than that achieved by cyanidation under similar test conditions ($2.5\,mg/cm^2\,h$ for 2 g/L NaCN) (Tran *et al.*, 2001). The stability of the Au(III) chloride complex ($AuCl_4^-$) is strongly dependent on the solution pH and requires high chloride and chlorine levels, increased temperature and high ore surface-area. The complex is only stable at $pH < 3.0$ unless a sodium chloride concentration higher than 100 g/L is maintained.

As the dissolved gold complex is unstable and re-precipitates upon contact with a reductant such as sulfidic materials or metals, application of the chloride–chlorine systems is limited to extraction of gold from oxidized materials. Attempts have been made to reduce the reactivity of sulfides in halide systems using compounds such as flotation collectors used to coat sulfides (Stace, 1984). This was found effective for some metals sulfides (*e.g.*, copper sulfides), where the coating significantly reduced their reactivity without altering the reaction rate of gold dissolution. Other sulfides such as pyrite were unsuccessful.

High silver contents in ores possibly dissolve slowly in low chloride solutions because of the formation of a passivating film of insoluble silver chloride (Sparrow and Woodcock, 1995). Consequently, higher concentrations of chloride in solution are required to solubilize the relatively insoluble silver chloride. Therefore, the chloride system is not ideally suited to treatment of ores in which silver is of primary value.

4.1.2. *Bromine*

Bromine-leaching results in rapid gold dissolution at near neutral pH conditions. Due to the high potential required for dissolution ($E^o = 0.97\,V$ vs. SHE), compared with the formation of gold cyanide at $-0.57\,V$ (vs. SHE), gold bromide is unstable and requires the addition of a strong oxidant such as bromine. Extensive research on the bromide–bromine system was carried out in the 1990s. Electrochemical techniques were applied by Pesic and Sergent (1992) and by van Meersbergen *et al.* (1993); to determine the complex reaction mechanism for gold dissolution in bromine–bromide systems. The dissolution of gold was shown to depend on the bromine–bromide ratio and the associated minerals in the ore. The presence of copper, zinc and aluminium as sulfates have no effect on dissolution, but iron(II) and manganese(II) are oxidized and consume bromine. Alternative oxidants to bromine to eliminate the problems associated with high vapour pressure and corrosive reactions of bromine have been examined with limited success. These are ferric ion, hydrogen peroxide and sodium hypochlorite (Trindade *et al.*, 1994; Sparrow and Woodcock, 1995). The use of commercially available organic bromides (*e.g.*, *N*-halo hydantoins such as Geobrom 3400), also reduce problems with vapour loss.

4.1.3. Iodine

Of all the halogens, the gold iodide complex is the most stable in aqueous solution, presumably because of its lower redox potential compared with the other halogens. Hiskey and co-workers have extensively evaluated the leaching behaviour and chemistry of gold and silver dissolution in various iodide–iodine mixtures (Hiskey and Atluri, 1988; Hiskey and Qi, 1991; Qi and Hiskey, 1991, 1993; Angelidis *et al.*, 1993). The gold dissolution rate was directly proportional to iodine and iodide concentrations and was not greatly affected by changes in pH over the range pH 2–10. Several early patents were granted on the application of this system for deep lead *in situ* leaching (McGrew and Murphy, 1985) or for processing gold from electronic scrap (Falanga and MacDonald, 1982). The iodide–iodine system does not normally oxidize metal sulfides such as chalcocite and pyrrhotite; therefore, avoiding excessive reagent consumption in a potential gold-processing plant (Hiskey and Qi, 1991). Consequently, it might be appropriate for treating ores containing sulfidic minerals. However, recovery and regeneration of the active species are important, as iodide and iodine are very expensive.

Alternative oxidants have been suggested in the iodine system such as hypochlorite permits a lower iodine concentration in solution, and so minimize losses of iodine by evaporation (Davis and Tran, 1992; Davis *et al.*, 1992). The conditions for extraction including oxidant/iodide molar ratio, concentration and pH have to be optimized to avoid the passivation of gold by gold iodide (AuI) and to maximize the gold extraction rate. In addition, hypochlorite concentration has to be properly optimized as an overdose of this oxidant can destroy the iodide lixiviant used for complexing gold. A maximum gold dissolution rate was achieved at a $[OCl^-]/[I^-]$ molar ratio of 0.25 (Davis and Tran, 1992). In this system, the active species dissolving gold is I_3^-, which is formed from the reaction between hypochlorite and iodide. The same applies for the hypochlorite–bromide system, in which the active species dissolving gold is Br_3^- (Tran *et al.*, 2001).

4.2. Halides – applications

Pre-treatment of sulfidic or carbonaceous ores by roasting or pressure oxidation is normally required prior to chlorine or bromine leaching to render ores relatively inert, and consequently reduce reagent consumption (Li *et al.*, 1992; Sparrow and Woodcock, 1995). For example, the selective recovery of gold and silver was carried out recently by Puvvada and Murthy (2000) from a chalcopyrite concentrate. Gold and silver grades in the concentrate were 11 and 140 g/t, respectively. Laboratory-scale tests were conducted at room temperature on 20% solids slurry containing 25 g/L NaOCl and 0.35 M HCl. Increasing the NaCl concentration increased the rate as well as the extent of gold and silver extraction. Gold and silver recoveries of 42.7 and 45.0%, respectively, were obtained with 200 g/L NaCl. Dissolution of silver was found to be independent of NaOCl concentration. However, pressure oxidizing the copper concentrate and then leaching with NaOCl concentration of 25 g/L, 200 g/L NaCl and 0.35 M HCl for 1 h resulted in gold and silver recoveries of 90.0 and 92.5%, respectively.

A pre-feasibility test on hypochlorite leaching McDonald Gold Mine oxide ore in Montana gave 68% gold recovery compared with the 73% obtained with cyanide (McNulty, 2001). Under the conditions used in their bottle-roll testwork (pH 6.5, Eh 1.14 V (vs. SHE), 33% solids (for 96 h leaching time) reagent consumption was 5.55 kg/t NaOCl and 3.25 kg/t HCl compared with 0.15 kg/t NaCN and 0.55 kg/t CaO for the cyanide process.

Interest in the use of chloride-based leaching for treating gold from copper anode slime has continued with several studies on its kinetics (Dönmez *et al.*, 1999; Herreros *et al.*, 1999). The technique was tested or practised in several copper refineries in the early 1990s (see Tran *et al.*, 2001 and references therein).

4.3. Halides – current status

Halide leaching provides greater flexibility than cyanidation as reagent dosages can be controlled to enhance the dissolution rate and is particularly useful for processing coarse gold in oxidized materials. However, gold halides are unstable and critics remain skeptical, as a great deal of chemical and process control is required during processing to maintain gold in solution. Furthermore, losses of bromide or iodide absorbed on gangue minerals or precipitated as insoluble copper silver or lead salts, can lead to high reagent consumptions for low-grade ore applications. The technique is suitable for extracting gold from gold-rich materials such as anode slimes and oxidized gravity-gold concentrates. Chlorination processes are being utilized as a gold- and silver-refining technique to replace smelting. The lack of a suitable recovery process to match the cyanide CIP plant technology has been the main limitation of the use of chloride systems for treatment of whole ores.

4.4. Other halide processes

4.4.1. The Minataur^{TM} process

The Minataur^{TM} process, developed by Mintek in South Africa, comprises oxidative leaching of the feed material, followed by selective solvent extraction of the gold from the leach liquor to reject impurities and precipitation of high-purity gold (Feather *et al.*, 1997). Suitable feeds include silver-refining anode slimes, gold-electrowinning cathode sludge, zinc-precipitation filtrates, gravity-gold concentrates and the residues from mill liners in gold plants. Impure gold feed material is leached for 2–3 h in 5 M HCl under oxidizing conditions with chlorine continuously added into the leach reactor. The leach solution is then purified by solvent extraction. Gold is selectively extracted into the organic phase (not specified) over silver as well as the platinum-group and base metals, which report to the raffinate. Gold is recovered as a metal powder by direct reduction in sulfur dioxide or oxalic acid from the loaded strip liquor. In addition, the Gravitaur^{TM} process has been developed that incorporates gravity concentrates as the feed, without the need for an intermediate solvent-extraction step to upgrade the gold tenor of the solution.

Chinese researchers (Li *et al.*, 1996) have also evaluated a chloridizing process for gold extraction from silver anode sludge, where gold is recovered by reduction of liquor with oxalic acid, possibly similar to the Minataur^{TM} process.

4.4.2. Intec gold process

The Intec Copper process is primarily used for processing copper and other base metal sulfides; however, the application to the simultaneous extraction and recovery of gold/silver has also been evaluated (Moyles, 1999). In this process, copper sulfide feeds are typically leached at 85°C using a chloride electrolyte (280 g/L NaCl and 28 g/L NaBr) containing a chlorine–bromine complex ($BrCl_2^-$, named *Halex*) produced from a copper-electrowinning cell downstream. It is expected that gold and silver will be easily leached by this leachant, which achieves a solution potential (Eh) of around 1.2 V (vs. SHE). Silver is recovered by cementation, whereas gold is recovered by precipitation as the solution potential is dropped to less than 0.80 V (vs. SHE) after leaching (Severs, 1999).

5. OXIDATIVE CHLORIDE LEACH PROCESSES

Besides chlorine, several other oxidants, such as oxygen or nitric acid, dissolve gold in the presence of chloride. Oxidative chloride leaching may have possible applications in treating silicate ores if only small amounts of high gold sulfide minerals are present, or it can be used as a total dissolution process for treating sulfide ores to recover base and precious metals. Most oxidative chloride leach processes, including ferric chloride leaching, have been mainly used as a pre-treatment process rather than a gold-leaching process. However, the Platsol® Process has been developed to leach and recover base metals, gold and PGMs from sulfide ore.

5.1. Oxidative chloride leach – process conditions

Some conditions used for leaching gold in chloride systems are listed in Table 4.

Except for special processing of high-grade materials, such as the refining of precious-metal concentrates, gold bullion or platinum metals, *aqua regia* is not considered practical for use at the plant-scale level. Suitable oxidants include oxygen under pressure, ferric salts, hydrogen peroxide, sodium hypochlorite and persulfates (Sparrow and Woodcock, 1995). While there has been renewed interest in the Haber process in recent years (Haber, 1988), which is believed to be halide-based, the actual conditions used in the process are not specified.

Acid ferric chloride solutions have been used primarily as a process to oxidize sulfide concentrates and complex lead–zinc sulfide ores and concentrates prior to cyanidation (*e.g.*, Jain and Hendrix, 1996). However, recent electrochemical investigations by Liu and Nicol (2002) have demonstrated the effectiveness of iron(III) as the oxidant for leaching of gold at high temperatures under typical pressure-oxidation conditions used for treating refractory gold ores. Measurements of the equilibrium potentials of the gold(III)/gold and iron(III)/iron(II) couples over a temperature range from 25 to 200°C in acidic sulfate solutions containing various concentrations of chloride ions showed that the equilibrium solubility of gold increases with increasing temperature, chloride concentration and iron(III)/iron(II) ratio.

Table 4
Typical oxidative chloride conditions used in leaching gold

Process	Ligand	Oxidant	Gold complex in solution	Typical leaching conditions	pH
Aqua regia	Cl^-	HNO_3	$AuCl_4^-$	3:1 $HCl:HNO_3$	<0
Ferric chloride	Cl^-	Fe^{3+}	$AuCl_4^-$	3–6% $FeCl_3$	<2
Platsol®	Cl^-	O_2 (689 kPa)	$AuCl_4^-$	5–10 g/L NaCl; >220°C	~2

5.1.1. Platsol® process

The Platsol® process was developed in collaboration with the University of British Columbia, Kane Consultants Ltd and Lakefield Research in Canada for the treatment of flotation sulfide concentrate for Polymet Mining Company in Minnesota. This process involved dissolution in one step of the base metals (copper and nickel) as well as the gold and PGMs. This was followed by solid/liquid separation, gold and PGM recovery and conventional Cu SX/EW and recycling of the copper raffinate to the autoclave. Pilot-plant work has been carried out.

The fundamental difference between the Platsol® process and the conventional high-temperature pressure-oxidation processes is that a small concentration of chloride ions is added to the autoclave with ~25 g/L sulfuric acid. The chloride favours the oxidation of gold and platinum-group metals and stabilizes them as dissolved chloro-complexes. Grinding the ore with ceramic rather than iron balls was required to prevent cementation of gold chloride (Ferron *et al.*, 2000).

The concentrate tested was a flotation concentrate assaying 14.7% Cu, 3.05% Ni, 0.14% Co, 26.7% S, 1.4 g/t Au, 2.2 g/t Pt and 9.9 g/t Pd. Pressure-oxidation conditions were 225°C, pulp density 11%, retention time 120 min and oxygen overpressure was 689 kPa. The ore treated had a P80 of 15 μm. After solid/liquor separation, the gold and PGMs were recovered by sulfide precipitation using NaSH or by activated carbon. The copper was recovered using conventional solvent extraction and electrowinning techniques. Overall recoveries were Cu 99.6%, Ni 98.9%, Co 96%, Pd 94.6%, Pt 96% and Au 89.4% (Ferron *et al.*, 2001). Recent work in treating a variety of refractory gold concentrates under optimum conditions (225°C, NaCl 10–20 g/L, 2–6 h O_2 at 700 kPa) achieved gold extractions of the order of 90–96% compared with direct cyanidation where gold extraction was less than 20% (Ferron *et al.*, 2003).

Examination of a variety of recovery options showed that loading of gold onto carbon from clear liquors and pulps was rapid and did not require prior neutralization. Zadra elution of the loaded carbon recovered more than 90% of the gold; however, further work in investigating carbon regeneration is required. Gold could easily be precipitated from acidic Platsol® leach liquors with NaSH, but minimization of the co-precipitation of impurities, such as copper, needed to be addressed. In addition, gold recovery by ion-exchange resins was considered. More details of the Platsol® process may be found in Chapter 35.

5.2. Oxidative chloride leach – current status

Most of these processes are restricted to high-grade concentrates and have been used as a pre-treatment process for leaching gold with cyanide. Similar to the halide systems, the stability of gold in solution and the lack of a suitable recovery option appear to restrict them as a simultaneous leaching and recovery process. For sulfide ores containing a combination of base, precious and platinum-group metals, these processes may be viable.

6. SULFIDE/BISULFIDE/SULFITE LEACHING

The sulfur-based gold lixiviants other than thiosulfate and thiourea are sulfide, bisulfide, bisulfite (or sulfur dioxide) and polysulfides. Of these possible lixiviants only the bisulfide and bisulfite ions appear to have any practical use under ambient conditions. YES Technologies (Hunter *et al.*, 1998) described a process using *bi*sulfide generated from sulfate-reducing bacteria as a lixiviant for gold, although *bi*sulfide ions can readily be generated from hydrogen sulfide gas. Alkaline sulfide lixiviation of sulfur residues from the Nitrogen Species Catalysed Pressure Leaching process (Anderson, 2003) has been demonstrated to leach and recover silver successfully.

6.1. Sulfide/bisulfide/sulfite leaching – process conditions

The possible processes investigated using sulfur-based lixiviants for gold are listed in Table 5. The mechanism of gold dissolution and precipitation from aqueous sulfide solutions under a range of conditions has received considerable attention in the early geological literature (*e.g.*, Hannington and Scott, 1989; Seward, 1973; Tan and Bell, 1990). Neutral *bi*sulfide solutions dissolve gold as follows:

$$\mathrm{Au} + \mathrm{H_2S} + \mathrm{HS^-} = \mathrm{Au(HS)_2^-} + 1/2\mathrm{H_2} \qquad (9)$$

Under weak acid conditions the neutral gold complex $\mathrm{Au(HS)^o}$ species forms, while under strongly alkaline conditions $\mathrm{Au_2(HS)_2S^{2-}}$ is formed (Seward, 1973). Because of the similar stabilities of gold and silver *bi*sulfide complexes, *bi*sulfide leaching may be suitable for leaching gold ores with significant silver content (Hunter *et al.*, 1998).

The YES process uses naturally occurring, sulfate-reducing bacteria for the recovery of gold and silver from ores. A full description of the process is outlined in the patent by Hunter *et al.* (1998). Conventional bio-oxidation of ore particles is carried out to free the precious metals dispersed or occluded within the ore. A portion of the acidic, base-metal sulfate leach solution produced from bio-oxidation is introduced to an anaerobic reactor. A non-toxic donor such as acetate or methanol (which does not bind to activated carbon) is added to the anaerobic reactor to enrich within it a mixed culture of sulfate-reducing bacteria. *Bi*sulfide ions are generated biologically in the

Table 5
Typical sulfur-based conditions used in leaching gold

Reagent	Ligand	Oxidant	Gold complex in solution	Typical leaching conditions
Sodium sulfide	HS^-	H_2S generated	$Au(HS)_2^-$	50 g/L Na_2S, $pH > 12$
YES technology (bacteria SO_4^{2-} reducing process)	HS^-	H_2S generated	$Au(HS)_2^-$	Around 2.5 g/L H_2S, HS^-, and S^{2-}, pH 6–9
*Bi*sulfite or SO_2	HSO_3^-	O_2	$Au(HSO_3)_2^-$	15–50 kg/t SO_2, pH 4–5
*Poly*sulfide	S_x^{2-}	S^o	Au/S_x	>2 M *poly*sulfides
Lime sulfur synthetic solution/ Phase transfer catalysts	$S_2O_3^{2-}$, S_x^{2-}	O_2, Cu(II) and NH_4^+	$Au(S_2O_3)_2^{3-}$, Au/ S_x(?)	?
Nitrogen species catalysed pressure leaching process	S_5^{2-}, $S_2O_3^{2-}$	NO^+, S^o	AuS_5^-; Au, $S_2O_3^-$	20–175 g/L H_2SO_4, 620–975 kPa, 125–170°C, 2.0 g/L HNO_3

process with an electron donor such as acetate by the following reaction;

$$CH_3COO^- + SO_4^{2-} \rightarrow 2HCO_3^- + HS^- \tag{10}$$

Additions of acidic sulfate solution may be required to maintain a neutral pH in the reactor. In a second process step, the submerged oxidized ore (to exclude oxygen) is leached by recirculating the neutral *bi*sulfide lixiviant, saturated with H_2S. Precious metals are recovered from the pregnant *bi*sulfide solution by contact with activated carbon or other conventional techniques.

Since HS^- ions and H_2S molecules diffuse more slowly than cyanide ions and oxygen molecules, slower gold dissolution can be expected than with cyanide leaching if the same concentrations of reactants are used. Possible problems with regard to obtaining high gold recoveries include passivation and adsorption effects, which are not well understood.

Investigations into using *poly*sulfides to leach gold have been carried out by Chen *et al.* (1996). Gold dissolution can occur as a result of adsorption of *poly*sulfide on gold surfaces accompanied by oxidation of *poly*sulfide as follows:

$$Au/S_x \rightarrow AuS^- + (x-1)S^o + e \tag{11}$$

$$Au/S_x \rightarrow Au/S_x + 2e \tag{12}$$

$$S^o + 2e \rightarrow S^{2-} \tag{13}$$

Chen *et al.* (1996) reported 90% gold extraction from a sulfide concentrate at 50°C without the addition of an oxidant. However, a relatively high *poly* sulfide concentration is required for high gold extraction. Similar processes where *poly*sulfide was generated *in situ* such as the *Lime/Sulfur Synthetic Solution* and *Phase Transfer Catalysts* have also been described (Deng *et al.*, 1984; Zhang *et al.*, 1993), but in this case thiosulfate is also present. In mixtures of thiosulfate and *poly*sulfides, the *poly*sulfides only act as a lixiviant when no other oxidant is present. In the presence of copper, *poly*sulfides precipitate with copper to form CuS.

6.1.1. Nitrogen species catalysed pressure leaching process

In the nitrogen species catalysed pressure leach process developed at Montana Technical University, the sulfur residue is converted into a gold extracting lixiviant (Anderson, 2003). The principles of the reaction of a sulfide mineral with nitric acid in conjunction with sulfuric acid are shown below. It is postulated that the actual reaction species is NO^+, and not NO_3^-, which reacts with the mineral and oxidizes the sulfide to sulfur at an Eh of around 1.45 V (vs. SHE).

$$2MeS_{(s)} + 4NO^+_{(aq)} \rightarrow 2Me^{2+}_{(aq)} + 2S^o + 4NO_{(g)} \tag{14}$$

By partially oxidizing the sulfide to elemental sulfur instead of sulfate, the gold can be accumulated in the elemental sulfur, recovered from the other leached solids and then leached via alkaline sulfide lixiviation, whereby the sulfur containing the gold is dissolved in an alkaline solution. The combination of sodium hydroxide and elemental sulfur results in the formation of sulfide (S^{2-}), sodium *poly*sulfide (Na_2S_x) and sodium thiosulfate ($Na_2S_2O_3$) as follows:

$$4S^o + 6NaOH \rightarrow 2Na_2S + Na_2S_2O_3 + 3H_2O \tag{15}$$

$$(x-1)S^o + Na_2S \rightarrow Na_2S_x \qquad (\text{where } x = 2-5) \tag{16}$$

The gold is leached by *poly*sulfide and thiosulfate as follows:

$$Au^o + S_5^{2-} \rightarrow AuS^- + 4S + e \tag{17}$$

$$Au^o + 2S_2O_3^{2-} \rightarrow Au(S_2O_3)_2^{3-} + e \tag{18}$$

The gold can be recovered by electrowinning, chemical precipitation, cementation, solvent extraction or ion exchange. The barren alkaline sulfide solution can be recycled for further gold leaching or processed with low-temperature oxidation to produce sodium sulfate. As such, it is claimed (Anderson, 2003) that there is no environmental or toxicological issue in the use of alkaline sulfide gold recovery.

6.2. Sulfide/*bi*sulfide/sulfite leaching – applications

*Bi*sulfide leaching is clearly more applicable to sulfidic ores rather than oxidized ores. Touro and Wiewiorowski (1992) described a process of steam heating to 35–45°C finely ground ore (50% solids) and then conditioning with 2–5 kg/t of H_2S gas to make a gold–sulfide complex. A chelating agent such as 0.5 kg/t EDTA may be added to complex the calcium. Sulfur dioxide (15–50 kg/t, depending on the carbonate content of the ore) was then injected into the pulp to reduce the pH to the optimum range of pH 4–5. The pulp was then air agitated to maintain an oxidizing atmosphere for 16–20 h in the presence of an ion-exchange resin to simultaneously dissolve the gold and transfer it to the resin. The loaded resin was finally screened from the pulp and treated to recover the gold and regenerate the resin. Gold recovery obtained was 80% compared with 30% by CIL cyanidation in some ores.

Initial *bi*sulfide-leaching tests using the YES process attained 25–31% gold extraction from a bio-oxidized Nevada ore compared with 88% by conventional cyanide leaching (Hunter *et al.*, 1998). At the same time, 39–81% silver was recovered compared to 86% with cyanide. However, tests conducted in a pressure vessel to allow higher *bi*sulfide concentrations gave 75% gold extraction.

Some applications of the nitrogen species catalysed pressure leach process to treat auriferous copper sulfide concentrates have been reported (*e.g.*, Anderson, 2003). Pre-oxidation of 100 g/L concentrate (ground to a P80 of 10 μm) was carried out with 175 g/L H_2SO_4 at 620 kPa and 125°C, in the presence of 2 g/L nitrogen species. This was followed by alkaline leaching, resulting in 98.3% gold extraction.

6.3. Sulfide/*bi*sulfide/sulfite leaching – current status

Further fundamental investigations on gold dissolution processes involving sulfur chemistry are required. A better understanding of the adsorption and precipitation reactions, which reduce gold extraction, also requires further investigation. The advantages the process offers over cyanidation include lower reagent costs and the potential ability to leach preg-robbing ores and other ores not amenable to cyanidation. It may also selectively leach precious metals from base-metal concentrates (Hunter *et al.*, 1998).

One of the limitations would seem to be the bio-reduction of sulfate ion using organic substrates for *bi*sulfide regeneration. The *bi*sulfide process is recyclable, but oxidation to sulfate is theoretically possible. A major drawback is that H_2S, which is also generated, has an occupational health standard very similar to HCN. Extremely long retention times and a closed system would be required.

The nitrogen species catalysed pressure leach process is less hazardous and has been successfully demonstrated at laboratory scale on silver ores. Further investigations on treating gold ores are required. The process is most probably better suited for the extraction of multi-elemental systems such as base and precious metals.

7. AMMONIA LEACHING

Ammonia is most commonly used as an additional reagent in cyanidation for copper-containing ore bodies (see Chapter 32). However, the laboratory use of ammonia alone as a lixiviant for refractory gold ores has been reported at high temperatures, as recently reviewed by Han (2001).

7.1. Ammonia – process conditions

Ammonia leaching of gold in the presence of an oxidant is carried out at temperatures between 100 and 300°C and 600–1000 kPa of pressure using 5–10 g/L copper(II) as oxidant, 5.5 M free ammonia and 0.5 M ammonium sulfate. Leaching times are short, around 1–4 h. At ambient temperatures gold is passivated and gold dissolution in ammonia solutions is observed only above 80°C (Meng and Han, 1993). The most effective oxidant for gold dissolution in ammoniacal solutions is Cu(II) as represented in the following reaction (Guan and Han, 1996):

$$\mathrm{Au} + \mathrm{Cu(NH_3)_4^{2+}} = \mathrm{Au(NH_3)_2^+} + \mathrm{Cu(NH_3)_2^+} \tag{19}$$

The dissolution rate of gold increases with increasing copper and ammonia concentrations provided that there is sufficient ammonia to complex copper. Optimum pH conditions appear to be around 9.5. Increasing the temperature also increases the gold dissolution rate.

Alternative and less effective oxidants include oxygen, hypochlorite, peroxide and Co(III). The oxidation of sulfides in the ore produces some thiosulfate that complicates the leaching process. The use of combined halogen and ammonia as a gold-leaching process has also been examined. High gold recoveries are achieved at <100°C with iodine, providing the best oxidant in terms of the rate of dissolution of precious metals (Han, 2001). Iodine (I_2) is a very effective oxidant (Peri *et al.*, 2001), where gold can react with ammonia in the presence of iodine as an oxidant to form gold-ammine:

$$2Au + I_2 + 4NH_3 = 2Au(NH_3)_2^+ + 2I^- \quad (20)$$

One of the advantages of such a reaction is the ability to regenerate iodine by reaction with oxygen. However, no published applications on the use of iodine as an oxidant have been found.

7.2. Ammonia – applications

Sulfidic and carbonaceous refractory ores have been successfully treated by the ammonia process (Han and Fuerstenau, 2000) with $>95\%$ gold extraction achieved in 2–4 h compared with $<70\%$ by conventional cyanidation.

7.3. Ammonia – current status

The capital and operating costs are the limiting factors in the implementation of this process, since high pressures and temperatures are required. Consequently, it would probably only be viable in isolated cases (*e.g.*, spent catalysts or very high-grade concentrates).

8. BACTERIAL AND NATURAL ACID LEACHING

Gold has been reported to be solubilized in biological or natural systems by a combination of microorganisms and amino acids such as glycine, in the presence of an oxidant. High gold recoveries have been reported using both amino and humic acids. However, the rate of gold dissolution is extremely slow and therefore could probably only be used in treating low-grade ores by a heap-leach process (Sparrow and Woodcock, 1995).

8.1. Bacterial and natural acid – conditions

Typical conditions for the direct leaching of gold with bacteria (not to be confused with the bacterial oxidation of sulfide ores, discussed in Chapter 16) and natural acids are listed in Table 6.

Dissolution of gold is enhanced by the addition of an oxidizing agent such as sodium peroxide and by the selective breeding of more active strains of organisms. The reaction of amino acids with gold in the presence of permanganate produces a complex anion containing the salt of the relevant acid linked to gold(I) through gold–nitrogen bonds. An example of a gold dissolution reaction using amino acid such as glycine as the ligand is as follows

$$4Au + 8NH_2CH_2COOH + 4NaOH + O_2 = 4Na[Au(NH_2CH_2COO)_2] + 6H_2O \quad (21)$$

Table 6
Typical direct bacterial-leaching conditions used for gold

Reagent	Ligand	Oxidant	Gold complex in solution	Typical leaching conditions	pH
Bacteria and natural acids	Amino acids	O_2 or $KMnO_4$	$[Au(CH_2NH_2COO)_2]^-$ and possibly gold glycine	3–5 g/L amino acids 3–5 g/L $KMnO_4$ and 1 g/L *mer*thiolate, fermentation fluid obtained from cultivation of *Bacillus Subtilis* strain III-5	9.5
Natural acids	Humic acids	$KMnO_4$		5 g/L humic acid 10–15 g/L alkali, 2–3 g/L $KMnO_4$	Acidic

Bacteria, most notably *Bacillus subtilis*, in the presence of amino acids such as glycine and an oxidant, have been shown to dissolve gold from ore samples. Groudev and Groudeva (1990) found that *Bacillus Subtilis* was the most active solubilizing bacterium among 18 varieties tested. The aurous gold complex is an anion containing the salt of the relevant organic acid. Groudev and Groudeva (1990) found that under optimum leaching conditions (5 g/L amino acid, minimum 3–10 g/L potassium permanganate, 1.0 g/L sodium *mer*thiolate, at pH 9.5, Eh > 0.5 V, 30°C), nearly 90% gold extraction was obtained in 3 days by agitation leaching, and 70% extraction in 150 days by percolation leaching.

Humic acid and other naturally occurring organic acids have been studied by the U.S. Geological Survey, as mobilizing agents for gold in acidic swampy environments. Low gold solubility and slow kinetics militate against commercial use of this phenomenon. Mineev and Syrtlanova (1984) reported that a solution containing 5 g/L humic acid and 10–15 g/L of alkali in the presence of 2–3 g/L $KMnO_4$ leached 44% of the gold from a quartz–carbonate ore by percolation leaching in 45 days. Leaching the ore in pachuca tanks gave 69% extraction in 96 h. Reagent consumptions were 2 kg/t humic acid, 0.7 kg/t $KMnO_4$ and 8 kg/t NaOH. They estimated from cost data that the system is economically viable for ores containing 1–2.5 g/t Au. Fan *et al.* (1992) also used humic acid and some unspecified additive when column leaching several ores. They appear to have obtained 40–80% gold extraction with humic acid over a 20-day period compared with 60–90% with cyanide.

The ability of plants to take up gold has been long recognized (Girling and Peterson, 1999). Gold can be taken up actively, by utilizing the plant metabolism, or passively, by means of the carbonyl functional groups on plant tissues. Gold ions from aqueous solutions were recovered and reduced to elemental gold colloids by alfalfa biomass (Gardea-Torresdey *et al.*, 1999).

The adsorption of gold(III) ions from solution by dead alfalfa tissues (*Medicago sativa*) is almost independent of pH, but increases with temperature (Gamez *et al*., 1999, 2000).

8.2. Bacterial and natural acid – current status

The processes are not well understood and consequently no practical process exists. This is an area where further studies should be carried out, particularly as the substances are generally non-toxic. Much work has been carried out on the use of microorganisms in the treatment of minerals and effluents and this is an area where active research is increasing. The uptake of gold by plants and the mobilization of gold in soils have been the subject of several investigations (*e.g*., Greene *et al*., 1986) and could ultimately have limited commercial application for a secondary recovery process.

9. THIOCYANATE LEACHING

Thiocyanate has been known for a long time to act as a lixiviant for gold. Early work examined acidic thiocyanate solutions to recover gold and uranium simultaneously from South African gold ores (Fleming, 1986). Several studies on leaching rates, mechanisms and thermodynamics of the thiocyanate system have been published by Monhemius and co-workers (Barbosa-Filho and Monhemius, 1994a–c; Monhemius and Ball, 1995).

9.1. Thiocyanate – conditions

Gold can be leached by 0.01–0.05 M thiocyanate at potentials of around 0.4–0.45 V at pH 1–3 in the presence of either ferric ions (2–5 g/L) or peroxide as oxidant. The simplified reaction can be written as follows:

$$\mathrm{Au} + 4\mathrm{SCN}^- + 3\mathrm{Fe}^{3+} = \mathrm{Au(SCN)}_4^- + 3\mathrm{Fe}^{2+} \tag{22}$$

Thermodynamic analyses indicated that at the upper limit of the potential range, $\mathrm{Au(SCN)}_4^-$ is to be the gold species formed but with decreasing potential, $\mathrm{Au(SCN)}_2^-$ is formed. It was proposed that intermediate species such as $\mathrm{(SCN)}_2$ and $\mathrm{(SCN)}_3^-$ act, like iodine, both as oxidants and complexants. In addition, various iron–thiocyanate complexes can also be present under certain conditions. More recently, Barbosa-Filho and Monhemius (1997) showed that thiocyanate can leach gold in the pH range of 1–3 at temperatures up to 85°C. However, increasing the pH of the thiocyanate-leaching solution has a detrimental effect on the gold dissolution rate (Kholmogorov *et al*., 2000), presumably because of Fe(III) hydrolysis.

Addition of small amounts of iodine or iodide has been shown to increase the rate of gold dissolution in the iron(III) thiocyanate system

(Barbosa-Filho and Monhemius, 1994d). This is most probably due to a synergistic effect as a result of the formation of iodine–thiocyanate species (such as I_2SCN^- and $I(SCN)_2^-$) (Monhemius and Ball, 1995).

Besides being destroyed by oxidation during leaching, thiocyanate is known to form complexes with several metal cations. For example, a precipitate is formed with copper in the leach solution (probably $Cu(CNS)_2$), and the blood-red ferric-thiocyanate complexes are formed with iron. While it may be possible to recirculate the thiocyanate in the iron complexes, the thiocyanate in the precipitated copper complexes would be lost from the circuit. Thus it can be expected that reagent consumptions would be significant.

9.2. Thiocyanate – applications

Kholmogorov *et al.* (2000) have recently investigated the use of thiocyanate solutions to extract gold from a chemically treated arsenopyrite concentrate. The concentrate, containing approximately 110 g/t gold, was leached at room temperature for 3–5 h with 39 g/L KSCN and 0.8 g/L Fe(III) at pH 2.2 and a pulp density of 5–10% solids. Gold extractions of 89–93% were achieved under these conditions. Comparative tests using 2.45 g/L NaCN at pH 11.3 resulted in 87% gold recovery in 89–96 h. Testwork on the pregnant leach solutions demonstrated that gold could be recovered by adsorption onto activated carbon and ion-exchange resins. Complete desorption of gold from resins was achieved by using sulfuric acid/thiourea solutions at room temperature and from activated carbon by using basic thiourea solution at 150°C.

Recently, both bottle-roll-leaching tests and column-extraction tests were carried out to assess the effect of thiocyanate and ferric ion concentrations on gold recovery from a bio-oxidized low-grade (2.13 g Au/t) refractory sulfidic ore from Nevada (Wan *et al.*, 2003). In bottle-roll tests conducted on ground bio-oxidized ore, the gold extraction after 24 h was 64% using 2.9 g/L SCN^- and 5.6 g/L Fe(III) (pH 2, 20% solids, $P80 = 75\,\mu m$). However, comparable cyanidation testwork gave 69% gold extraction. Increasing the initial ferric ion concentration had little effect on the gold dissolution, and thiocyanate degradation was observed to be rapid in the initial contact with ore. For the column tests, the bio-oxidized ore was crushed to −38.2 mm. After 16 days of thiocyanate treatment, gold extraction was 52% and 10% higher than that obtained with cyanide. However, thiocyanate consumption (0.6–0.8 kg/t of ore) was twice as high as cyanide consumption (0.33 kg/t of ore).

9.3. Thiocyanate – current status

This lixiviant may be suitable for most ore types and recycling of the leach solution could be possible. Unfortunately, in practice, interference reactions of sulfide minerals and other metal ions may require the use of higher temperatures to achieve satisfactory leach performance and may also cause significant decomposition. The low pH and higher temperatures would likely result in high capital costs and high operating costs compared to cyanidation. The limited availability of thiocyanate is also a restriction and if thiocyanate had to be detoxified by oxidation to cyanate and sulfate, it would further increase the operating costs.

10. RECOVERY PROCESSES

While this section is mainly concerned with the leaching processes, equally important is the selection of a method to recover gold. A major disadvantage of replacing cyanide with an alternative lixiviant remains that no suitable recovery of gold from solution has yet been conclusively demonstrated as economic.

Most research has been carried out on thiosulfate; thiourea- and halide-leaching systems with gold recovery by cementation, solvent extraction, carbon, ion-exchange resin or electrowinning techniques being investigated. A comprehensive review of options for gold recovery from non-cyanide solutions was first presented by Wan *et al.* (1993). Possible recovery options from thiosulfate solutions have been reviewed also by Grosse *et al.* (2003) and by Aylmore and Muir (2001), and are discussed in more detail in Chapter 22. In general, precipitation methods have been considered for clarified leach solutions, particularly from heap leaching, while carbon and resins have been considered for adsorption from slurries. Solvent extraction can generally only be applied to clarified solutions containing relatively high concentrations of gold and silver.

Work by Cashion and co-workers at Monash University in Melbourne have developed and demonstrated carbons with properties that result in the loading of gold from halide systems as the halide complex and not as metallic gold (Cashion *et al.*, 1997). This development in carbon technology potentially enables carbon to be used to recover gold from halide systems, with the carbon being stripped and reused. Unfortunately, the carbon used is soft and therefore not abrasion-resistant. In addition, no research in real pulp slurries or on the effect of impurities and recycling of carbon has been carried out to date. Modified carbons for recovery of gold from halides systems are thus still in the development stage.

11. ECONOMIC EVALUATION

To justify a mining project using an alternative lixiviant to cyanide, a complete financial analysis covering capital investment, operating expenses, revenue, water treatment and monitoring is required. However, it is difficult to obtain a complete picture of how different reagents respond to different ores due to the lack of detailed information in the published literature and limited pilot-plant data.

Table 7 shows comparative investigations carried out by several authors illustrating the variation in conditions, reagent consumptions and gold extractions observed in treating specific ores with different reagent systems. Clearly, the high reagent concentrations associated with the use of alternative lixiviants results in higher reagent consumptions compared with cyanidation. In cases where cyanide consumption is high, *e.g.*, the reaction of cyanide with limonitic gangue, alternative lixiviants can be more favourable than cyanide for leaching gold (Monhemius and Ball, 1995). Although some alternative reagents can give better gold extractions with carbonaceous or refractory gold ores, cyanidation often achieves the highest gold recovery. For high-grade ores, the economic benefit of increased gold recovery usually outweighs reagent cost and increased recovery is the main driver for choosing a particular system.

Table 8 shows the author's estimate of reagent cost for leaching a low-grade oxide ore (3.2 g/t Au, 0.3 g/t Ag, 0.5% pyrite in quartz/albite/clinochlore/biotite) in the Kalgoorlie region of Australia using cyanide and three other lixiviants based on optimum reagent compositions and estimated ranges of reagent consumption.

Without taking into account any differences in gold extraction, the reagent costs for thiosulfate are about double those for cyanide. While actual costs may vary, reagent costs for thiourea and chloride are estimated to be an order of magnitude higher than for cyanide or thiosulfate. These estimates indicate that in treating a low-grade ore, alternative reagent costs can be more expensive than the value of the gold.

In many cases, reduced reagent consumption is achieved when a pre-treatment process has been applied. Fleming *et al.* (2003) considered that pressure leaching followed by thiosulfate leaching was possibly economic, although in this case the variability of the ore caused significant differences in gold recovery. High reagent consumptions can obviously be tolerated where ores are refractory to cyanide, such as preg-robbing carbonaceous ores. Gold recoveries on the order of 60–80% using thiosulfate can be achieved, whereas cyanide extractions range from 0 to 15% (Wan *et al.*, 1994; Aylmore, unpublished).

An economic evaluation of all processes considered by McNulty (2001), which took into account the transport of reagents required for the leaching operations, revealed cyanide as the only option where a profit could be made by heap leaching at the McDonald gold mine. In addition, from the experience of Newmont Mining, additional costs would be associated with

Table 7
Comparison of leach investigations on selected ores

	Reagent concentrations (g/L)	pH	Reagent consumption (kg/t)	Au, Ag extraction (%)
Oxide ore (0.9 g/t Au, 5 g/t Ag), bottle-roll tests (McNulty, 2001)				
Cyanidation	NaCN = 0.5	10.5–11.0	NaCN = 0.15 CaO = 0.55	73, 23
Thiourea	$CS(NH_2)_2 = 2$	1.1–1.3	$CS(NH_2)_2 = 3.05$ $Fe_2(SO_4)_3 = 9.0$ $H_2SO_4 = 48$	57, 22
Thiosulfate	$(NH_4)_2S_2O_3 = 15$ $NH_4OH = 3.5$ $CuSO_4 \cdot 5H_2O = 0.06$	9.5	$(NH_4)_2S_2O_3 = 14$ $NH_3 = 2$	37, 16
Chloride	NaOCl = 1 NaCl = 100	6.4–6.5	NaOCl = 5.55 HCl = 3.25	68, 22
Bromide	$Br_2 = 1$ NaBr = 10	1.3–2.0	$Br_2 = 2.85$ $H_2SO_4 = 6.8$	57, 13
High-grade ore (68.2 g/t Au, 2 g/t Ag) (Monhemius and Ball, 1995)				
Cyanidation	NaCN = 5	10.5	NaCN = 7.80 CaO = 2.0	86
Thiourea	$CS(NH_2)_2 = 3.8$ $Fe_2(SO_4)_3 = 10$	1.5	–	<60
Thiocyanate	NaSCN = 8.1 $Fe_2(SO_4)_3 = 11$ $I_2 = 0.5$	2	NaSCN = 1.3	94

Table 7 (*continued*)

	Reagent concentrations (g/L)	pH	Reagent consumption (kg/t)	Au, Ag extraction (%)
Low-grade ore (4.8 g/t Au, 2 g/t Ag) (Monhemius and Ball, 1995)				
Cyanidation	NaCN = 5	10.5	NaCN = 7.42 CaO = 5.0	97
Thiourea	$CS(NH_2)_2 = 40$ $Fe_2(SO_4)_3 = 10$	2.5	$CS(NH_2)_2 = 12.8$	83
Thiocyanate	NaSCN = 8.1 $Fe_2(SO_4)_3 = 11$ $I_2 = 0.5$	2	NaSCN = 0.54	95
Sulfide ore (7.8 g/t Au, 13.4 g/t Ag, 11.2% S) (Munoz and Miller, 2000)				
Cyanidation	NaCN = 0.98	11	NaCN = 0.36	94
Thiourea	$CS(NH_2)_2 = 11.4$ $Fe_2(SO_4)_3 = 4$	2	$CS(NH_2)_2 = 38.3$	28
Thiocyanate	NaSCN = 8 $Fe_2(SO_4)_3 = 16$	2	NaSCN = 1.1	49

continuously shifting the heap to maintain chemical control for alternative lixiviants, which would increase both capital and operating costs. By comparison, consecutive heaps can be placed on top of one another in cyanide heap leaching operations.

12. ENVIRONMENTAL CONCERNS

The environmental properties of the alternative lixiviants to cyanide have also been considered in a number of articles (*e.g.*, Avraamides, 1982; Swaminathan *et al.*, 1993; DeVries and Hiskey, 1992). However, generally the process development work involving alternative reagents to cyanide

Table 8
Comparative reagent costs for treating a Kalgoorlie oxide ore

	Cyanide	Thiosulfate	Thiourea	Chlorine
Assuming mining/grinding costs fixed				
Leaching (40% solids)				
Reagent costs[a] *(A\$)*				
Lixiviant	NaCN \$1.61/kg	$(NH_4)_2S_2O_3$ \$0.75/kg	$CS(NH_2)_2$ \$3.5/kg	NaCl \$0.50/kg
Lime	\$140/t	\$140/t	–	–
Acid	–	–	\$150/t	\$150/t
Oxidant	\$0.80/m^3 (O_2)	\$0.43/kg ($CuSO_4$)	\$0.30/kg ($Fe_2(SO_4)_3$)	\$2.00/kg (NaOCl)
Others		\$0.50/kg (NH_3)	\$1.00/kg Na_2SO_3	
Reagent concentrations				
pH	10	9.5	3	5–6
Lixiviant	300–350 mg/L	6.6 g/L $S_2O_3^{2-}$	3.7–8 g/L	30 g/L NaCl
Lime	9.1			–
Acid	–	–	H_2SO_4	3.1 g/L HCl
Oxidant	15 mg/L	64 mg/L Cu as $CuSO_4$	Fe from ore	3.15 g/L NaOCl
Others		6.8 g/L total NH_3/NH_4^+	0–9 kg/t $NaHSO_3$	
Temperature	Ambient			
Reagent Consumption (kg/t of ore)				
Lixiviant	0.54 kg/t	2–3.4 kg/t $S_2O_3^{2-}$	3–8.4 kg/t	75 kg/t
Lime (Quicklime 81% CaO)	2.2	2	–	–
Acid	–	–	12–52 kg/t	13.4 kg/t
Oxidant	0.06 m^3/t	0.05–0.06 kg/t Cu	8.04 kg/t Fe	13.6 kg/t Cl^-
Others		1–1.5 kg/t NH_3/NH_4^+	0–5 kg/t $NaHSO_3$	
Costs based on reagent consumption (A\$/t$_{ore}$)				
Reagent costs	1.23	2.5–3.6	14.4–39.2	29.2–66.7

[a] Costs based on transporting chemicals to Kalgoorlie in 2001.

has mostly lacked any environmental focus in terms of consideration of regulatory factors, employee health and safety, environmental protection, proper disposal of wastes and sustainable development, all issues that mining companies would have to address.

DeVries and Hiskey (1992) first reviewed environmental implications of some of the alternative reagents to cyanide. The worker and environmental risks of the reagents used as alternatives to cyanide have been evaluated in detail by Gos and Rubo (2000). De Voto and McNulty (2001) have also emphasized the less than favourable environmental aspects of several of the alternative lixiviants. Many issues relating to environmental concerns with respect to the use of any of the lixiviants, including cyanide, will be based on local climatic conditions. Acid production in tailings dams (especially after decommissioning) is possibly the real threat to the environment, irrespective of leaching process used, although the acidic-leaching processes such as thiourea and halide will likely be more severe than others.

While studies have investigated the effect of cyanide in the environment, no studies on the effect of alternative lixiviants on the environment could be found. This is primarily as a result of the fact that there are no commercial alternative processes. However, sufficient investigations on other mineral processes are available, which provide enough information to indicate that some of these alternatives, such as those using ammonia, are more of an occupational health and safety as well as an environmental concern than cyanide. This has been illustrated by Gos and Rubo (2000).

A major aspect of minimizing the worker and environmental risk would be selection of a process that minimizes the quantity of chemicals used. Since many of the alternative lixiviants use around 50 times the concentration used in cyanide leaching, it is important to be able to recycle as much reagent as possible, not only to reduce costs to the leaching process, but also to prevent build up of dissolved and precipitated solids in tailings dams. Methods for reagent recycling or destruction of cyanide have been demonstrated to be successful on economic and environmental grounds, and many have been utilized in the mining industry. However, while some alternative reagents to cyanide can be recycled, such as through adsorption on carbon or resins, further investigations are required.

13. CONCLUSIONS

Of all the processes available, thiosulfate and chloride leaching appear to be the most favourable options to replace cyanide. However, in developing an alternative process, reductions in reagent consumption and improvements in recovering gold from solution are required. Feasibility studies into the worker and environmental risks associated with the process will undoubtedly have to be taken into account before commercialization, particularly in environmentally sensitive areas.

Extensive investigations of thiosulfate or thiourea as alternative lixiviants to cyanide at semi-commercial scale have been carried out by both Newmont and Barrick Gold. This is not because of any particular concerns with the environment or health and safety concerns while using the cyanide system, but because cyanide is unable to effectively extract gold from a proportion of their carbonaceous ore resources.

Oxidative chloride-leaching and chlorination processes have been used extensively as pre-treatment processes to oxidize refractory or carbonaceous ores prior to conventional cyanidation and carbon-in-pulp technology, rather than as a gold leach process. While high gold dissolution by halides has been demonstrated, improvements in gold recovery methods are required before direct gold recovery from such processes can become a reality.

Despite pilot-plant trials on many of the alternative options to cyanide, none have been successfully commercialized to any significant degree. Many of the pilot-scale studies have highlighted problems associated with scaling up a new technology from laboratory experiments to pilot-plant or commercial stage:

- Halides, thiourea and thiosulfate leaching are very susceptible to variations in mineralogy of the feed being leached and may require constant adjustments in regulating reagent concentrations to maintain optimum leaching conditions.
- Except for halogens, most alternative reagents do not exhibit fast leach kinetics compared with cyanide at similar concentrations.
- Shortfalls in reagent recovery and in gold recovery are evident when running a continuous leaching operation due to adsorption or reaction with other ore minerals.
- Conditions in heap-leach operations on a large scale are more difficult to maintain compared with cyanide and are not easily scaled up from column leach experiments in the laboratory.
- Higher reagent concentrations compared to that used in cyanide leaching, make recycling important to make gold extraction by alternative lixiviants economical.
- The complexity of the process is substantially greater than in cyanide leaching.

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Chapter 22

Thiosulfate as an alternative lixiviant to cyanide for gold ores

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Ammoniacal thiosulfate is an attractive alternative reagent to cyanide for processing gold ores (see Chapter 21 for discussion of various other alternative lixiviants). It is relatively cheap and non-toxic, forms relatively strong gold and silver complexes and readily leaches gold ores when catalysed by Cu(II). It is particularly suited to carbonaceous ores where the recovery of gold by cyanide is poor. However, research over the past 30 years has identified a number of chemical and practical issues that must be understood and overcome before an overall process can economically rival cyanide for typical oxidized gold ores.

This chapter reviews recent advances in our understanding of the chemistry and mechanism of gold dissolution, as well as fundamental studies on the passivation of the gold surface. The speciation and stability of the thiosulfate system is considered under typical leaching conditions, together with examples of leaching various gold ores that have been reported in the literature. Some of the areas that require further research include decreasing the oxidation of thiosulfate by Cu(II) or oxygen, alternative oxidants, overcoming the passivation of gold, increasing the extraction of gold compared to cyanide and understanding the variation in gold recovery between ores. More work is also required to minimize the effect of polythionates on gold recovery using resins or alternative absorbents and to recycle or minimize the concentrations of reagents used.

1. INTRODUCTION

The perceived and real environmental concerns and pressures when dealing with cyanide solutions and waste streams in sensitive areas, has an impact on

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the sustainability of the whole gold industry. Although the North American gold processing industry has recorded only three deaths attributed to cyanide over a period of 100 years (McNulty, 2001), the public media remembers the 14 major incidents throughout the world over the past 25 years – 10 involving tailings dams, two involving pipeline failures and two involving transportation accidents. Increasing regulatory scrutiny of new gold projects and a lowering of what is considered acceptable levels of cyanide discharges are of considerable concern to the industry, making approval for any new gold project using cyanide extremely difficult in some parts of the world. In these cases, the political and environmental cost of using cyanide becomes too much and the establishment of an economic and environmentally viable option for extracting gold without the use of cyanide would seem essential. For this reason, the gold industry has been seriously looking at thiosulfate as the safest and cleanest reagent that not only meets chemical criteria, but also toxicological and most environmental criteria.

Research and development over the past 20 years has focused on understanding and applying the copper-catalysed ammoniacal thiosulfate system to carbonaceous ores and copper–gold ores where gold recovery is poor when using cyanide, or cyanide consumption is high. Recent reviews by Aylmore and Muir (2001a) and by Grosse *et al.* (2003) provide extensive references on the various ores that have been studied and discuss the thermodynamics, speciation and mechanism of leaching as well as the stability of thiosulfate and the various gold recovery options. Over the past 5 years, much more basic research has been carried out at Monash University on the electrochemistry and kinetics of gold leaching (*e.g.*, Breuer and Jeffrey, 2003a), while research groups at the University of British Columbia and the A.J. Parker CRC for Hydrometallurgy have applied and developed more knowledge on the leaching of various copper–gold ores and oxide gold ores provided by companies (*e.g.*, Molleman and Dreisinger, 2002; AMIRA, 2003). Much of this work is unpublished, like the research also carried out by Newmont, Placer-Dome and Barrick. These companies in particular have carried out extensive investigations on finely ground slurries of carbonaceous ores and pressure-leach residues as well as heap leaching of low-grade carbonaceous ores, sometimes to semi-commercial scale (Wan *et al.*, 1995; Wan, 1997; Wan and LeVier, 2003; Fleming *et al.*, 2003).

Unfortunately, no overall process has been piloted or costed using thiosulfate with typical oxidized gold ores, because the overall gold recovery is generally lower and reagent consumption is higher compared to cyanide. There are also issues and impediments to the recovery of gold from thiosulfate leach solutions using anion-exchange resins, which makes resins less effective than carbon in cyanide-leach solutions (Nicol and O'Malley, 2001, 2002; Zhang and Dreisinger, 2002a; Muir and Aylmore, 2004). This chapter therefore considers recent advances in our understanding of the process chemistry and mechanism in various studies on leaching gold ores with thiosulfate. Some of the issues and impediments that must be overcome before a viable and economic process can replace cyanide are also considered. The recovery of gold from thiosulfate solutions is discussed in more detail in Section 3.

2. THIOSULFATE CHEMISTRY

2.1. Mechanism of gold leaching

The oxidation of metallic gold to the aurous Au^+ ion in 0.10 M ammoniacal thiosulfate in the presence of copper(II) occurs at a potential of about 0 V (vs. standard hydrogen electrode, SHE) and can be represented by Eq. (1). However, recent studies by Senanayake (2004) suggest that the mechanism involves the formation and absorption of a mixed copper(II)–ammonia–thiosulfate complex on the gold surface with simultaneous oxidation of gold and thiosulfate. Copper(II) is a catalyst for this reaction at concentrations around 10^{-3}–10^{-4} M (6–60 mg/L), with oxygen acting to re-oxidize copper(I) to copper(II) according to Eq. (2).

$$2Au + 10S_2O_3^{2-} + 2Cu(NH_3)_4^{2+} \rightarrow 2Au(S_2O_3)_2^{3-} + 8NH_3 + 2Cu(S_2O_3)_3^{5-} \quad (1)$$

$$2Cu(S_2O_3)_3^{5-} + 8NH_3 + \tfrac{1}{2}O_2 + H_2O \rightarrow 2Cu(NH_3)_4^{2+} + 2OH^- + 6S_2O_3^{2-} \quad (2)$$

Over the years, many researchers have accepted the view that gold initially forms the ammonia complex $Au(NH_3)_2^+$ on the gold surface, and this species then undergoes ligand exchange with thiosulfate. This view is largely based upon the similar stability constants for the ammine and thiosulfate complexes published in the literature. However, recent evidence from Senanayake *et al.* (2003) indicates that the ammine complex is 9–11 orders of magnitude less stable than the thiosulfate complex and hence is an unlikely intermediate. Thus ammonia is not directly involved in the mechanism of leaching gold except as a complexant for copper(II).

An electrochemical study by Breuer and Jeffrey (2002) confirms that the reduction of copper(II) ammine to copper(I) thiosulfate occurs readily in the potential region where gold is oxidized. Unfortunately, both oxygen and copper(II) also oxidize thiosulfate to trithionate and tetrathionate, resulting in high consumption of the reagent and the production of other species that impair gold leaching (see below). Other studies by Breuer and Jeffrey (2003b) have shown that the oxidation of thiosulfate in the presence of both copper(II) and oxygen is surprisingly complex, with oxygen increasing the rate of thiosulfate oxidation and copper(II) reduction. It is believed that thiosulfate is oxidized by both copper(II) – via an intermediate complex – and by a copper(I)–oxygen radical species. Anions such as chloride and phosphate significantly lower the rate of copper(II) reduction by thiosulfate, while polythionates such as tetrathionate greatly increase the rate of reduction (Breuer and Jeffrey, 2003c).

The calculated standard reduction potential of the cuprous–cupric couple in ammoniacal solution and thiosulfate lies between 0.14 and 0.36 V (SHE), depending upon the reagent composition and predominant species present (Table 1). The table also demonstrates that this redox couple has a sufficiently high potential to oxidize thiosulfate to tetrathionate. Because copper(II) is rapidly reduced by thiosulfate to copper(I), an equilibrium ratio of Cu(II)/Cu(I) is established, which depends upon the relative concentrations of ammonia and thiosulfate and dissolved oxygen.

Fig. 1 shows the effect of Eh and ammonia concentration on copper speciation in dilute (0.10 M) ammonia thiosulfate solutions (Aylmore and Muir, 2001b). It is clear from Fig. 1 that the optimum Eh/pH window for stabilizing Cu(II) and leaching gold becomes very small with dilute reagents. In 0.10 M $NH_3/S_2O_3^{2-}$ solutions the calculated solubility of Cu(II) is $\sim 5 \times 10^{-3}$ M Cu(II) at the optimum Eh and pH around 250–300 mV (SHE) and 9–10, respectively. At higher pH and Eh values, copper precipitates from solution as tenorite [CuO], but this re-dissolves with increasing ammonia. Increasing the ammonia concentration significantly increases the ratio of Cu(II)/Cu(I) species in equilibrium, while an excess of thiosulfate

Table 1
Standard reduction potential for copper(II) ammonia/copper(I) thiosulfate and thiosulfate/tetrathionate couples

Couple	Standard reduction potential (V)
$Cu(NH_3)_4^{2+}/Cu(S_2O_3)_3^{5-}$	0.22
$Cu(NH_3)_4^{2+}/Cu(S_2O_3)_2^{3-}$	0.14
$Cu(NH_3)_3^{2+}/Cu(S_2O_3)_3^{5-}$	0.36
$Cu(NH_3)_3^{2+}/Cu(S_2O_3)_2^{3-}$	0.27
$S_4O_6^{2-}/S_2O_3^{2-}$	0.12

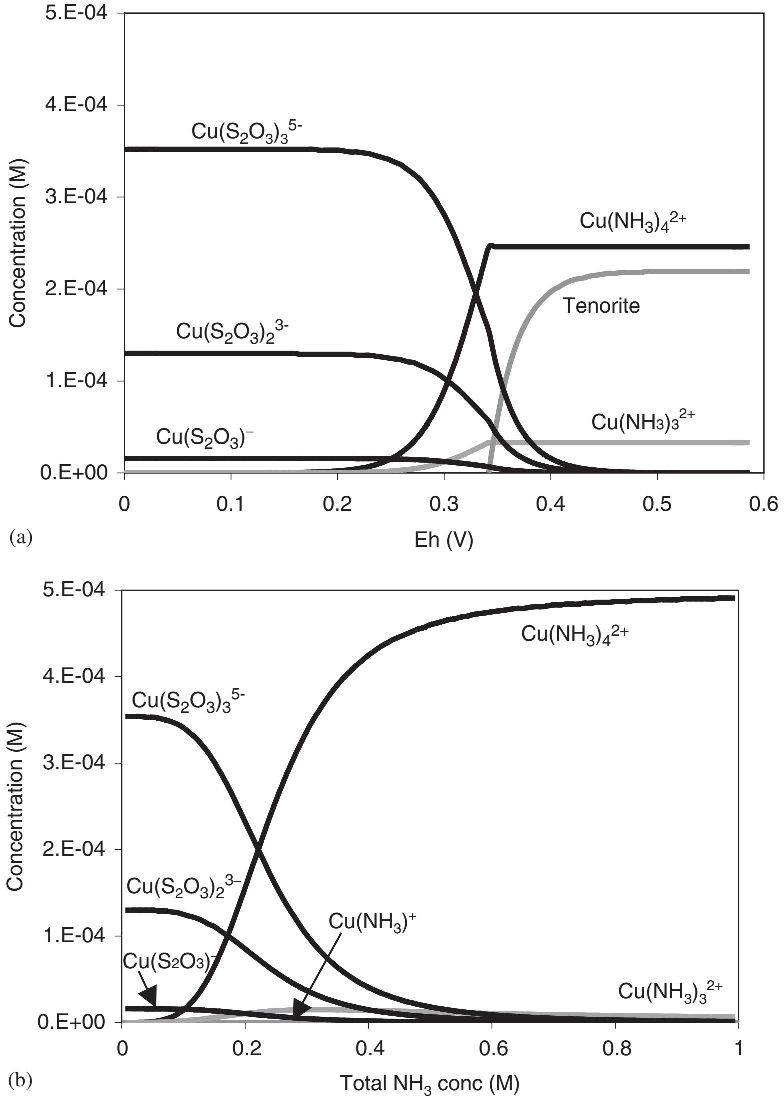

Fig. 1. (a). Distribution of copper species at different Eh conditions for low reagent concentrations (0.1 M $S_2O_3^{2-}$, 0.1 M NH_3, 5×10^{-4} M Cu, pH 9.5). (b) NH_3 conditions in 0.10 M thiosulfate solution (5×10^{-4} M Cu, pH 9.5, Eh = 0.250 V assuming pK_a of $NH_4^+ = 9.5$).

relative to ammonia drives the equilibrium to favour $Cu(S_2O_3)_3^{5-}$ species. Thus much closer control of leaching conditions must be maintained compared to cyanide, and the ratio of ammonia/thiosulfate must be > 1 to ensure that sufficient Cu(II) moeities are present.

Lam and Dreisinger (2003) discuss the importance of maintaining sufficient $Cu(NH_3)_4^{2+}$ in solution to leach gold and how this species is affected by changes in pH, temperature and thiosulfate concentration. As thiosulfate gets oxidized to tetrathionate and polythionates, the ratio of Cu(II)/Cu(I) increases. Yet, despite rising levels of Cu(II) during a typical leach, gold extraction stops after about 6 h, with some re-precipitation of gold from solution.

2.2. Kinetics of gold leaching

A recent series of papers by Jeffrey *et al.* (2001), Breuer *et al.* (2001), Breuer and Jeffrey (2002) and Jeffrey (2001) discuss the fundamental kinetic and electrochemical aspects of gold and silver leaching with ammoniacal thiosulfate, and compare alternative lixiviants such as cyanide and chloride/hypochlorite. In general, the initial rate of leaching with 0.1 M thiosulfate containing 10 mM Cu(II) and 0.4 M NH_3 was similar to the rate with air-saturated 5 mM cyanide (250 mg/L NaCN), and significantly slower than 5 mM hypochlorite solution. The rate was dependent upon copper(II), thiosulfate and ammonia and was faster with higher concentrations of the reagent. Unfortunately, reagent degradation was also much faster, and this led to a decrease in the leach rate owing to passivation of the gold surface by some unidentified reaction products (Breuer and Jeffrey, 2002). Fundamental rotating disc studies by Aylmore and Rae (2001) established that the initial degradation products tetrathionate and trithionate had no effect on leaching rate, which prompted further investigations as discussed below.

Recent studies on gold colloid kinetics in ammoniacal thiosulfate solutions (Zhang *et al.*, 2004) showed the oxygen–cyanide system to be significantly faster than the copper(II)-catalysed thiosulfate system, which in turn was much faster than the oxygen–thiosulfate system. Surprisingly, in the absence of copper(II), an increase in the ammonia or oxygen concentration resulted in a decrease in the initial rate of gold dissolution. But increasing ammonia concentrations gave a higher overall recovery of gold. Thus, even the colloid showed evidence of passivation in solutions containing 50 mM $S_2O_3^{2-}$/ 0.2 M NH_4^+/0.25 mM O_2 at pH 9.5, with the kinetics following a shrinking core model under mixed chemical-diffusion control ($E_a = 25 - 37$ kJ/mol).

Other studies by Chu *et al.* (2003) rather strikingly revealed that increasing oxygen concentrations severely impaired the leaching of gold, despite its role in regenerating copper(II). This was attributed to the presence of disulfite ($S_2O_5^{2-}$) produced as an intermediate in the free-radical oxidation of copper(I) by O_2. Addition of disulfite to the leach solution resulted in very low rates of gold leaching. Faster leaching and longer delays before passivation were observed when reacting gold powder or an oxide gold ore with minimum oxygen addition to maintain steady-state Cu(II) and Eh values (Jeffrey *et al.*, 2003).

A more fundamental and wider-ranging study on the effects of various additives on the rate of electrochemical oxidation of gold was subsequently carried out by Chandra and Jeffrey (2004), using a rotating electrochemical quartz-crystal microbalance (REQCM). This revealed some interesting and unusual features. It was shown that several organic sulfur- or nitrogen-containing species such as xanthate, pyridine, dithiocarbamate and imidazole completely passivated gold oxidation in thiosulfate solutions, while thiourea and thioacetamide enhanced oxidation. Similarly, ammonium and alkyl ammonium cations increased the rate of gold oxidation compared to sodium and other alkali cations. Curiously, a 2% silver–gold alloy electrode was more active than gold in pure thiosulfate solutions but was less active in the presence of thiourea. Other studies by Chandra and Jeffrey (2003), which included an investigation of the rate of cathodic oxygen reduction on gold, found that the presence of 5 mg/L Pb or Bi increased the rate of oxygen reduction, but in the presence of both Pb and thiourea the overall rate of gold oxidation was hardly changed in an oxygen-saturated thiosulfate solution.

The summary review by Breuer and Jeffrey (2003a) of the chemistry, electrochemistry and kinetics of gold leaching in oxygenated copper–ammonia–thiosulfate solutions highlights the complexity and limitations of the system and the need to consider other additives or oxidant systems. Surface absorption of oxidized thiosulfate species appears to play a critical role in the kinetics and passivation of gold in thiosulfate solutions that are difficult to control and define. Various sulfur-containing species arising from the oxidation of thiosulfate and decomposition of polythionates are likely to absorb strongly unless more selective species such as thiourea are present in sufficient concentration. Ammonia appears to inhibit the absorption or formation of these species on the gold surface although its exact role is unclear.

2.3. Decomposition of thiosulfate and polythionates

One of the major problems in thiosulfate leaching of gold ores is the high consumption of thiosulfate reagent during gold leaching and the generation of polythionates, which readily absorb on anion-exchange resins and impair the recovery of gold from solution. Ji *et al.* (2003) demonstrated that to achieve gold loadings on resin similar to that on carbon from the cyanide system, the level of polythionates has to be reduced to below 0.1 g/L. In typical leach solutions containing about 1 g/L polythionates, the ratio of gold-on-resin/gold-in-solution was less than 1000 (Ji *et al.*, 2003; Nicol and O'Malley, 2001, 2002).

High consumption of thiosulfate is mainly caused by its oxidation in solution, although losses by absorption onto ore minerals or bacterial degradation cannot be ruled out. Thiosulfate is a metastable anion that can undergo chemical decomposition depending upon the Eh and pH of the solution and the presence of copper acting as a catalyst. The Eh–pH diagram for the metastable S–H_2O system has been reported by Kametani and Aoki (1976) and Osseo-Asare (1989), in which the thermodynamically most stable species (*i.e.*, HSO_4^- and SO_4^{2-}) are omitted to reveal the metastability domain of species such as thiosulfate ($S_2O_3^{2-}$), tetrathionate ($S_4O_6^{2-}$) and sulfite (SO_3^{2-}).

Under alkaline conditions, a number of metastable sulfur species, such as sulfite (SO_3^{2-}), thiosulfate ($S_2O_3^{2-}$), dithionate ($S_4O_6^{2-}$), trithionate, tetrathionate, sulfide and polysulfides ($S_n{}^{2-}$) are found, depending on Eh. Some of the many reversible reactions in which thiosulfate is either consumed or regenerated are discussed by Aylmore and Muir (2001a) and by Grosse *et al.* (2003). Thus the sulfur–water system is complicated because sulfur is multivalent and easily forms sulfur–sulfur bonds and higher-order species. However, sulfate is the ultimate thermodynamically stable species under gold-leaching conditions.

It can be seen that the stability region of $S_2O_3^{2-}$ is restricted to a narrow range of Eh in neutral to basic pH solutions and oxidizes to tetrathionate between pH 4 and 10 when catalysed by Cu(II), as illustrated by Eq. (3). Tetrathionate itself is unstable at pH >10 (see Eq. (4)). However, in the presence of oxygen, direct oxidation of thiosulfate to sulfate and trithionate also occurs:

$$8S_2O_3^{2-} + 2Cu(NH_3)_4^{2+} \rightarrow 2Cu(S_2O_3)_3^{5-} + S_4O_6^{2-} + 8NH_3 \tag{3}$$

$$4S_4O_6^{2-} + 6OH^- \rightarrow 5S_2O_3^{2-} + 2S_3O_6^{2-} + 3H_2O \tag{4}$$

Fundamental studies by Byerley *et al.* (1973a, b, 1975) on the kinetics and mechanism of oxidation of thiosulfate ion in aqueous ammonia solution, established that the rate of oxidation and uptake of oxygen was dependent upon the concentration of Cu(II) and thiosulfate, and was inversely proportional to ammonia concentration. Other studies on the kinetics of decomposition of tetrathionate and trithionate in alkaline solution (Naito *et al.*, 1970; Rolla and Chakrabarti, 1982; Zhang and Dreisinger, 2002b) showed that while tetrathionate can be readily decomposed to thiosulfate and trithionate by raising the pH value to 11 (Eq. (4)), trithionate was more stable and required an unacceptably high pH value or temperature to effect decomposition. This has practical significance because even trithionate alone impairs the recovery of gold using resins, as noted above.

According to Naito *et al.* (1970) and Byerley *et al.* (1973a), under non-oxidizing conditions, over half of the oxidized thiosulfate can be regenerated slowly from the decomposition of tetrathionate via sulfite and higher polythionate ions. The reaction is catalysed by the presence of thiosulfate ions according to the reaction scheme:

$$S_4O_6^{2-} + S_2O_3^{2-} \rightarrow S_5O_6^{2-} + SO_3^{2-} \tag{5a}$$

$$SO_3^{2-} + S_4O_6^{2-} \rightarrow S_3O_6^{2-} + S_2O_3^{2-} \tag{5b}$$

$$S_5O_6^{2-} + 3OH^- \rightarrow 5/2S_2O_3^{2-} + 3/2H_2O \tag{5c}$$

$$2S_4O_6^{2-} + 3OH^- \rightarrow 5/2S_2O_3^{2-} + S_3O_6^{2-} + 3/2H_2O \tag{5}$$

However, studies by Miura and Koh (1983) indicate that tetrathionate decomposes to thiosulfate and sulfite ion together with sulfoxylic acid ($S(OH)_2$) and some sulfide ion:

$$10S_4O_6^{2-} + 20OH^- \rightarrow 10S_2O_3^{2-} + 10S(OH)_2 + 10SO_3^{2-} \tag{6a}$$

$$6S(OH)_2 + 6OH^- \rightarrow 3S_2O_3^{2-} + 9H_2O \tag{6b}$$

$$4S(OH)_2 + 8OH^- \rightarrow 4/3S^{2-} + 8/3SO_3^{2-} + 8H_2O \tag{6c}$$

$$10S_4O_6^{2-} + 34OH^- \rightarrow 13S_2O_3^{2-} + 38/3SO_3^{2-} + 4/3S^{2-} + 17H_2O \tag{6}$$

Several researchers have reported that the reaction between Cu(II) and thiosulfate slowly produces some Cu_2S or CuS (Rubai and Epstein, 1992; Abbruzzese *et al.*, 1995), which lends support to this latter reaction. Furthermore, Fleming *et al.* (2003) demonstrated that addition of NaHS to leach solutions not only precipitated copper but also partially or completely precipitated the gold.

Interestingly, the presence of sulfite ions has been claimed to prevent the formation of any free sulfide ion and avoid the precipitation of gold or silver from solution. In early research, Kerley (1983) reported that maintaining a level of 0.05% sulfite ion stabilizes the thiosulfate in solution. However, recent studies by Fleming *et al.* (2003) and Ji *et al.* (2003) found that sulfite addition after leaching, reacted with the tetrathionate that had built up to form trithionate, sulfate and thiosulfate. Of course, too much sulfite addition will stop gold leaching by consuming oxygen and reducing Cu(II).

Clearly, the mechanism and decomposition pathway of thiosulfate and tetrathionate species are complex and not well understood, and depend upon

Eh and pH. There is evidence that some copper and silver sulfide can precipitate from solution, which could also contain gold, but the exact mechanism for gold losses from solution is not simple. There is also evidence that controlled addition of sulfite ion could be beneficial both in removing trace sulfide and/or tetrathionate and in controlling excess oxygen and Cu(II), which are detrimental to leaching. Thus, much closer control is required in the copper-catalysed ammoniacal thiosulfate system to prevent undesirable side reactions.

2.4. Passivation of gold

Despite the obvious passivation of gold that occurs after several hours of leaching in thiosulfate solutions, and the passivating effect of certain additives discussed above, the exact mechanism and form of the passivating film is poorly understood. Bagdasaryan *et al.* (1983) and Wan and LeVier (2003) observed a "sulfur layer as well as copper sulfide" when leaching gold foil in a thiosulfate–copper sulfate system. However, neither the XRD nor Raman spectra matched exactly with pure sulfur. Fundamental electrochemical studies by Pedraza *et al.* (1988) in neutral sodium thiosulfate solution indicated the formation of a sulfur-like film. Other electrochemical impedence spectral studies in sodium thiosulfate solutions in the absence of copper suggest that amorphous elemental sulfur may be formed, preventing thiosulfate from diffusing to the gold surface (Chen *et al.*, 1996; MacDonald, 1990).

Recent electrochemical studies by Zhang and Nicol (2003) in alkaline thiosulfate solutions again found evidence for a sulfur-like film, which largely disappeared in the presence of ammonia. However, there was no evidence that gold was complexed by ammonia under these conditions. Furthermore, the coulombic efficiency of gold dissolution was only about 0.6, reflecting a competitive oxidation reaction on the gold surface. The general belief is that an elemental sulfur-like coating is formed either by the adsorption of elemental sulfur formed in the double layer, or by the oxidation of sulfide ion produced by the decomposition of oxidized thiosulfate species absorbed on the gold surface. The role of ammonia is to minimize surface coverage of this sulfur-like film.

3. LEACHING STUDIES WITH AMMONIACAL THIOSULFATE

3.1. Background and recent studies

A review of the literature (Aylmore and Muir, 2001a) shows that thiosulfate has been used on several occasions to leach gold and silver ores since 1900, but serious interest did not take place until around 1980, with an emphasis on copper–gold and carbonaceous ores that give poor gold recoveries using cyanide. The earlier studies, using relatively high concentrations of reagents, gave reasonably high gold extractions but consumed thiosulfate up to 40 kg/t of ore.

It was recognized that it was necessary to limit the concentration of copper in solution because Cu(II) degrades thiosulfate, leading to high reagent losses. Later studies by Langhans *et al.* (1992) established that comparable extraction of gold could be achieved with dilute ammoniacal thiosulfate and identified the catalytic role played by trace amounts of copper. Subsequent work carried out by Newmont (Wan *et al.*, 1995; Wan, 1997; Wan and LeVier, 2003) showed that it was possible to heap leach low-grade carbonaceous ores using dilute ammoniacal thiosulfate solutions with reasonable reagent consumptions (thiosulfate ~2–4 kg/t). In both cases, no more than 0.2 M thiosulfate and ammonia were used for leaching with about 60 mg/L Cu(II) as catalyst. However, it was not possible to assess the efficiency of this leach since high gold recoveries can never be achieved by heap leaching and a comparison with cyanide is not possible with carbonaceous ores.

In recent years, several research groups have studied copper–gold ores but generally find it difficult to control the extent of copper leaching and the degradation of thiosulfate (Molleman and Dreisinger, 2002). Typically, 20–50% Cu is extracted together with 50–85% Au, while reagent consumption varies from 10 to 40 kg/t. Control of aeration is regarded as critical to minimize reagent consumption. Studies by Freitas *et al.* (2001) on three Brazilian copper–gold ores found that each ore responded differently, and each required different leach conditions for optimum recovery of between 70 and 90% Au. In some cases, copper partially precipitated from solution and gold extraction reached a maximum after 8 h. Other recent studies by Xia *et al.* (2003) on a mildly refractory copper–gold ore achieved gold extractions around 90% but with a reagent consumption around 30 kg/t. Lower reagent consumption (< 10 kg/t) was achieved by increasing the pulp density; lowering the oxygen supply, adding sulfite ion; by complexing Cu(II) with ethylene diammine tetra-acetate (EDTA) or ammonium triacetate; or by replacing copper sulfate with nickel sulfate. The most significant factors were pulp density and oxygen flow.

Pressure-leached arsenopyrite ores from Barrick have also been examined by Lakefield Research, which carried out a large number of stirred tank tests at pH 8–9. Up to 95% Au was extracted from the finely divided gold left in the oxidized residue, but generally gold recovery varied from 50 to 95% (Thomas *et al.*, 1998). Likewise, studies made by the authors of this chapter on some relatively simple Australian oxide ores showed that while most of the gold and silver were readily leached in 2–4 h using a range of dilute reagent compositions, a fraction of the cyanide-soluble gold always remained in the thiosulfate leach residue (Table 2) (Muir and Aylmore, 2004). Although changes in reagent composition and leach conditions affected the

Table 2
Leaching studies on Australian oxide ores using dilute ammoniacal thiosulfate

Ore	Grade (g/t)	CN soluble (%)	Au recovery (%)	Ag recovery (%)
N. Queensland A (oxide)	21 (Au)	95	77–90	75–95
	15 (Ag)	88		
N. Queensland B (oxide)	11 (Au)	95	66–85	51–83
	10 (Ag)	95		
W.A. Goldfields (oxide + 1% sulfide)	3.8 (Au)	83	58–69	44–60
	2.8 (Ag)	67		
W.A. Goldfields (saline water/oxide)	3.3 (Au)	96	25–35	50–65
	0.3 (Ag)	>90		
N. Territory (oxide/gravity tail)	1.1 (Au)	90	58	ND

After Muir and Aylmore (2004)

kinetics and gold recovery, no conditions were found that could match gold recovery by cyanide. Furthermore, the recovery of gold from different ores varied even when similar leach conditions were used (Table 2), indicating that other factors are more important, as discussed below.

3.2. Factors affecting gold recovery and optimum reagent composition

Low gold recoveries from ores have been attributed to coarse gold, the precipitation of gold on iron from grinding media (Ji *et al.*, 2003) and the *preg-robbing* of gold onto sulfide and clay minerals (Feng and van Deventer, 2001; Aylmore and Rae, 2003; see Chapter 38). Sulfide minerals like arsenopyrite [FeAsS], pyrrhotite [$Fe_{(1-x)}S$] and pyrite [FeS_2] are also leached in ammoniacal thiosulfate (Feng and van Deventer, 2002), and hence consume oxygen/copper(II) and lower the Eh value. In some leach tests, over an extended time there has been evidence of re-precipitation of gold, silver and copper and lower gold recovery. Briones and Lapidus (1998) found that precipitation of Ag_2S occurred at low thiosulfate concentrations. Once Ag_2S is formed, it appears that dilute thiosulfate solutions can only partially re-leach the sulfide when the Eh value is increased. Of course, the decomposition of thiosulfate and passivation of the gold surface also leads to unacceptably long leach times and the poor recovery of coarse and occluded gold.

Overall, there appears to be no agreed optimum composition for leaching gold ores in the ammoniacal thiosulfate system. This is particularly evident when using dilute reagent compositions, as each ore appears to require a different blend of copper, ammonia, dissolved oxygen and thiosulfate to maximize gold recovery. This can be attributed in part to the different mineralogy and surface area, and the different absorption/reactivity of copper and reagent species on the gangue mineral surfaces. High reagent concentrations overcome this problem, but have unacceptable reagent consumption and pose economic and environmental concerns for any future plant.

3.3. Environmental issues

Although thiosulfate is generally regarded as relatively non-toxic, it is also metastable and can decompose either to polythionates and sulfate while consuming oxygen, or to toxic sulfide ion under anaerobic or reducing conditions. Thus its uncontrolled release into the environment poses problems of de-oxygenation of waterways or the potential formation of toxic species. While this can be avoided by oxidation of thiosulfate to sulfate prior to release, the cost of oxidation is likely to be much higher than the oxidation of cyanide due to the relatively high concentration of thiosulfate used and the moles of oxygen required (Gos and Rubo, 2000). Thus to be economic, it is necessary to minimize the release of thiosulfate and recycle as much as possible. But since recycling will build up polythionates in solution, it becomes important to leach gold with the minimum of thiosulfate.

Ammonia also poses environmental and toxic problems both as a gas in air and as a soluble solution. In air, the threshold limiting value (TLV) for ammonia gas is 14 mg/m^3 (Gos and Rubo, 2000), which is classified similar to HCN. In water, free ammonia is classified similar to chlorine, while ammonium ion has low toxicity. Unfortunately, ammonia is difficult to break down and may eventually metabolize to nitrate, which has the potential to promote algae growth and to pollute ground water. Hence, even stricter precautions have to be taken to control ammonia emissions from tanks or heaps, and to prevent its release into the environment.

3.4. Alternative thiosulfate systems

In order to overcome the environmental and economic problems of ammonia and the chemical problems of copper(II) degradation of thiosulfate, Ji *et al.* (2003) examined a novel ammonia and copper-free, oxygen–thiosulfate system. It was found that >80% Au was readily leached in less than 6 h at elevated temperatures (60–80°C) and overpressures of oxygen (10–100 psig) from the preg-robbing carbonaceous ore tested. Under these conditions there was relatively little degradation of thiosulfate; trithionate was the predominate product which could be significantly reduced by the addition of sulfite or by anaerobic decomposition at 90°C. Unfortunately, some gold re-precipitated during such treatments, while other work showed that gold passivation was more severe in the absence of ammonia (Zhang and Nicol, 2003). More work is required on this potentially attractive system to establish its viability to other ores.

Recent applied studies by Arima *et al.* (2004) have examined nickel as an alternative catalyst to copper in ammoniacal thiosulfate solution. It was found that up to 95% of the gold could be leached from a silicate gold ore using 10^{-4}–5×10^{-3} M Ni(II) as catalyst. Thiosulfate consumption was significantly lower (1–5 kg/t) compared to that with Cu(II) as catalyst, but the ammonia concentration was high (0.50 M, pH 9.5). It was proposed that Ni_3O_4 is produced on the gold surface and acts as the oxidant under the Eh and pH conditions of the leach. Other fundamental studies on alternative copper(II) ligands found that amino acids, polyamines and pyridine compounds inhibited thiosulfate degradation compared to ammonia (Brown *et al.*, 2003; Michel and Frenay, 1999) but clearly their application to ores is limited.

Other studies by Chandra and Jeffrey (2005) are focusing on using ferric oxalate as an oxidant at pH 4–6 in place of ammoniacal copper(II). Basic studies with a rotating gold-plated quartz disc show promisingly high leach rates in the presence of thiourea as catalyst, although, like the copper system, the rate slows with solution ageing. The mole ratio of ferric/oxalate and hence Eh proves to be an important factor. However, its application to ores is yet to be determined.

4. SUMMARY AND CONCLUSIONS

Table 3 summarizes the issues and impediments discussed above with regard to the thiosulfate leaching of gold ores, the recovery of gold from solution, the stability of the reagents and their release to the air or water. Clearly, there are some significant technical problems for a continuous operation, such as the presence of tramp iron in the grinding circuit and difficulties in recycling the tailings solution to the grinding circuit. Not all the issues can be solved, but all impediments must be addressed and understood before an overall process can be developed, tested and costed.

There is no doubt that, despite its shortcomings, thiosulfate is an attractive alternative to cyanide for processing carbonaceous ores where the recovery of gold is poor. It may also be attractive for processing some refractory copper–gold concentrates and ores that consume significant cyanide. However, for simple oxide ores, further research is required on alternative oxidants and

Table 3
Summary of issues and impediments associated with thiosulfate leaching of gold ores and recovery from solution

Aspects	Issues	Impediments
Kinetics and mechanism	Cu(II) oxidizes both Au and S_2O_3	High reagent consumption
	Complex leach kinetics	Copper in ore difficult to control; dependent on Cu(II), T, NH_3, S_2O_3
	Chemically controlled	Passivation of gold surface
	Ag_2S partially leached	Au associated with Ag_2S not leached
Reagents	Relatively high [S_2O_3]	Cost of reagents
	Excess NH_3 is required to minimize Au passivation	Recycling builds up impurities
	Relatively low [Cu(II)] required	Effluent treatment cost high
		NH_3 moderately hazardous
		Cu(II) absorbed on minerals
Stability	Thiosulfate oxidized to polythionate	Possible precipitation of Au/Ag/Cu sulfide
	Polythionates unstable	
pH	Controls free NH_3, Cu(II), Eh	Recovery sensitive to pH near 9.5
	High pH decomposes thiosulfate and tetrathionate	Possible precipitation of sulfides
Dissolved oxygen	Controls Cu(II), Eh	Recovery sensitive to DO
	Oxidizes thiosulfate to trithionate	High reagent consumption
Temperature	Slow kinetics at 20°C	Recovery sensitive to temperature
	Reagent degradation >40°C	
Time	Rate of oxidation S_2O_3 remains constant while gold extraction slows	Build up of polythionates for small increase in gold
Gold deportment	Coarse gold and gold in sulfide minerals slow to leach	Long leach time builds up polythionates
Ore mineralogy	Possible preg-robbing of copper and gold by clays	Recovery sensitive to ore type and mineralogy
	Reactive sulfides consume O_2/Cu(II)	Leaching impaired or stopped
	Grinding iron from milling ore	Metallic iron precipitates Cu and Au

Table 3 (*continued*)

Aspects	Issues	Impediments
Precipitation of gold	Copper and silver co-precipitation with gold	Loss of gold or cost of precipitate re-leach
Recovery on resins	Polythionates co-absorb on SB resin	Low resin loading increases cost
	Copper absorbs on resin	Copper competes for gold Possible precipitation of sulfides in resin
Elution of resin	Separation of Cu and polythionates	Two stage elution required
	Recycling of eluant	Impurity control

additives to overcome passivation to improve gold recovery and lower reagent costs to match that of cyanide.

Until some of these issues are overcome, there is little current economic incentive to switch existing plants from cyanide to thiosulfate, except for the processing of carbonaceous ores. However, the threat of increasing public concerns over cyanide management will ensure that companies will continue to strive for a viable alternative. The industry's first endeavour with the thiosulfate system is to develop a robust overall process flowsheet that can be realistically used and costed for a range of actual ores – including gold recovery, reagent recycling or destruction and impurity control.

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II.5 *Gold Recovery*

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Chapter 23

Carbon-in-pulp

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1. INTRODUCTION

The use of cyanide to leach gold ores revolutionized the gold industry at the beginning of the 20th century, providing a new process that was efficient, cost-effective and widely applicable. The introduction of activated carbon to recover gold from cyanide leach solutions in the last quarter of the 20th century had a similar impact on the economics of gold ore processing. By replacing the Merrill–Crowe zinc cementation step, carbon-in-pulp (CIP) and carbon-in-leach (CIL) recovery provided a process that allowed the treatment of lower grade and problematic ores (*e.g.* high-clay ores), at lower capital and operating costs and higher metal recoveries.

In a fortuitous bit of timing, this technology became available as the world gold industry entered a period of unparalleled expansion following the deregulation of the gold price in the mid-1970s. As a consequence, in a relatively short period of 10–15 years, the new technology was developed, proven and implemented industry wide.

1.1. Early history of carbon use in gold recovery

Although the era of CIP commenced in the late 1970s, the use of carbon for the recovery of gold was recognized and practiced much earlier. Davis (1880)

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patented the use of wood charcoal for gold recovery from chlorination leach liquors, with this process subsequently used at Mount Morgan, Australia in the early 1890s. Johnson (1894) patented the use of wood charcoal for the recovery of gold from cyanide solutions. Charcoal was employed in the late 19th century for the recovery of gold from cyanide-leach liquors in Victoria, Australia (Mactear, 1897; Gross and Scott, 1927). At the Yuanmi Gold Mine in Western Australia zinc precipitation was replaced by charcoal for a time commencing in 1916. In these earlier applications the gold was typically recovered by burning of the charcoal, with pulverized charcoal being used to recover the gold from solution.

In 1927, Gross and Scott of the US Bureau of Mines published an extensive report on the use of charcoal to recover gold and silver from cyanide solution, identifying many of the key parameters of the process (Gross and Scott, 1927). Their study included the investigation of a wide range of chemical systems for the elution of the precious metals from loaded charcoal. Although they identified sodium sulfide, sodium cyanide and sodium hydroxide as chemicals that aided elution, an efficient and practical elution process remained a serious impediment to wider application of the process. As further improvements in the zinc precipitation option were introduced, charcoal was largely abandoned.

1.2. The modern era of CIP

The modern application of activated carbon as an alternative to the Merrill–Crowe process had its genesis in the post-war years in the United States. The first CIP flowsheet was introduced at the Carlton Mill, Cripple Creek, Colorado (Fast, 1988) in 1951, employing an elution process relying on ammonia complexation of the gold, which had been developed by Merrill (of Merrill–Crowe fame). Around the same time, an alternative elution process involving sodium sulfide had been developed by Zadra (1950). Subsequently, Zadra *et al.* (1952) developed an elution process using caustic cyanide with integrated electrowinning, which would ultimately become the first truly successful, commercial elution process (Zadra Process). It was tested at the San Andreas Mine (Zadra *et al.*, 1952) and would eventually replace the ammonia process at the Carlton Mill. With the installation of the Zadra elution process at the CIP plant at the Homestake Mine in South Dakota in 1973 (Fast, 1988), all the essential elements of the modern CIP process were now in place.

The first modern CIP plant in Australia was commissioned in 1975 at Canbelego, New South Wales, to retreat 6 g/t surface tailings from the old Canbelego mine. It was not a financial success. Several other small operations followed, until 1981 when a number of CIP plants were commissioned starting with the Haveluck plant of Whim Creek Consolidated (Close, 2002).

In South Africa the first CIP plant was commissioned in 1978 at Modderfontein 74 (Bailey, 1987). This was followed by more than a dozen plants between 1980 and 1983, treating a range of feeds.

By the late 1980s, most of the equipment and processes that today characterize CIP technology were in place. By 2000, several hundred plants had been built.

2. ACTIVATED CARBON

The majority of the activated carbon used for precious metal recovery is either granular coconut-shell carbon or peat-based extruded carbon. Important considerations when selecting an activated carbon for use in a CIP operation include gold-loading kinetics (activity), gold-loading capacity, elution kinetics, level to which gold can be eluted, strength and abrasion resistance, particle-size distribution and wet density.

The properties of a particular activated-carbon sample will have a significant impact on most aspects of the gold-recovery operation, affecting variables such as carbon inventory, residence times, gold losses, carbon losses and elution conditions. Therefore, due consideration must be given to the physical and chemical properties of the virgin carbon when selecting a particular brand for precious-metal recovery.

2.1. Carbon assessment methods

In addition to standard ASTM (American Society for Testing and Materials; now ASTM International) procedures (see ASTM D 2652-76, 1976), most activated-carbon manufacturers have their own in-house procedures for testing their product and normally provide comprehensive data sheets for their customers. Unfortunately, these test methods usually vary between manufacturers. A number of more important methods are detailed below.

2.1.1. Kinetic activity

Several different methods for monitoring the rate at which gold is adsorbed on to carbon from an alkaline cyanide solution have been proposed (Avraamides, 1989). Differences in procedure include equipment employed (agitated baffled vessels, bottle rolls, flask shaker), solution composition, carbon preparation, carbon concentration, carbon particle-size and test duration.

Essentially, all the procedures involve contacting a known mass of carbon with a solution of known initial gold concentration, collecting and analysing samples of the solution over a period of time and then calculating the activity of the carbon sample based on the data obtained.

Unfortunately, there is currently no accepted standard method for evaluating carbon activity. A number of the test methods are summarized in Table 1.

- Parker Centre method (modified Mintek method – Fleming *et al.*, 1980).
- Tennant Ltd method (Follis, 1992).
- Mintek method (Shipman, 1994).
- Calgon Corporation method (Faulkner *et al.*, 1987).
- Pica Pty Ltd method (Pica Activated Carbon Aust. Pty Ltd, 1996).
- Sutcliffe Speakman (Sutcliffe Speakman Carbons Ltd).

It should be noted that the first-order rate equation, upon which most of the calculations of a rate constant are based, does not apply when the carbon is near equilibrium and when solution grades of the test liquor are depleted (Smith *et al.*, 1984). Although the data often fit the equation well for the first hour of the test, when carbon loading becomes excessive or when solution grades are too low, the determined rate constant starts to decrease and the collated data will not fit the rate equation (La Brooy *et al.*, 1986). In tests where plant carbons are being evaluated, the procedures will often include a sample of fresh (virgin) carbon, with a relative activity calculated by setting the fresh carbon to 100%.

The AMIRA P420A Gold Industry Survey of Australasian mining operations (Barbetti *et al.*, 2000) showed that many gold-mining operations used a single-point activity test for on-site carbon evaluation. Although several different methods were reported, all involve the collection of a single solution sample at the end of the test and the use of a simple ratio equation to calculate activity relative to a fresh carbon standard.

McArthur *et al.* (1987) suggest that when selecting carbon for CIP circuits, the activity of the carbon should be determined after it has undergone a period of attritioning. The more active component will be lost during attritioning and the activity of the carbon will drop as a result, producing data that is more representative of the plant situation.

Follis (1992) advocated measuring activity test samples by volume rather than by mass in order to avoid mass variations due to the presence of adsorbed contaminants. A badly fouled circuit-carbon sample will contain less carbon than an equivalent mass of virgin carbon and, consequently, the activity test data can be misinterpreted. It has also been suggested that, in order to obtain more reliable results, activity tests should be conducted in plant process water rather than in tap or distilled water. Results from one investigation showed that 30–50% slower kinetics were found in clear hypersaline solutions relative to distilled water (La Brooy, 1991).

Table 1
Kinetic activity test parameters for selected multiple-point methods

	Parker Centre	Tennant Ltd	Mintek	Calgon corp	PICA Pty Ltd	Sutcliffe Speakman
Carbon variables						
Drying temperature (°C)	25[a]	150	110	?[d]	110	105[c]
Drying time (h)	As required	> 4	> 12	?	?	To constant mass
Size range (mm)	2.00–2.36	2.00–2.36	1.7–2.00	2.00–2.36	As received	2.00–2.36
Mass (g)	0.5	5.00 (mL)[b]	1.00	1.7	1.00	1.00
Solution variables						
Initial [Au] (mg/L)	10	100	20	5	10	10
Volume (L)	0.5	0.51	0.4	1.7	1.0	1.0
pH	10.0	10.5	10.0	10.0	Natural	10.0
Buffering	None	Borate	Borate	Borate	None	Borate
$CaCl_2$ added (mg/L)	None	None	None	None	100	275
Alkali added	NaOH	NaOH	NaOH	?	None	NaOH
[NaCN] (mg/L)	250	None	None	?	100 (as KCN)	250 (as KCN)
Test conditions						
Pre-wet carbon	No	Yes	No	?	No	Yes
duration (h)	3	0.33	1.5	2	1	1.5
Sampling (min)	30, 60, 120, 180	1, 5, 10, 15, 20	15, 30, 45, 60, 75, 90	?	10, 20, 30, 40, 50, 60	15, 30, 45, 60, 75, 90
Agitation	Bottle roll	Overhead stirrer	Bottle roll	Overhead stirrer	Overhead stirrer	Linear shaker
Speed	100	300 rpm	50 rpm	400 rpm	200 rpm	130 oscillations/min

[a] The as-received sample is air-dried before use. Moisture content is determined by drying at 110°C to calculate the true carbon mass.

[b] The apparent density of the carbon is determined and the mass of carbon equivalent to 5.00 mL is used in the test.

[c] Carbon is boiled in dilute HCl and water washed before drying.

[d] Data not available.

2.1.2. Gold-loading capacity

The gold-loading capacity of an activated carbon, often referred to as the K value, is determined from an adsorption isotherm and is defined as the equilibrium loading on carbon in contact with 1 mg/L Au solution. Most methods (for example, Parker Centre method (AMIRA Project 83/P173A, 1987), Mintek method (Shipman, 1994), Norit method (Osei-Agyemang, 1992) Anglo American Research Laboratories method (Davidson *et al.*, 1982)) involve contacting varying masses of pulverized carbon with a volume of gold cyanide solution for 20 h or more.

The approach used by Pica Activated Carbon Aust. Pty Ltd (1996) is different. In the Pica procedure, a sample of carbon is contacted for 1 h with 1 L of 10 mg/L gold solution. Residual gold in solution is measured, and gold adsorbed on to the carbon is calculated as $G1$. The carbon is recovered and put into a new fresh batch of 10 mg/L gold solution for a further hour. Gold adsorbed on to the carbon is calculated as $G2$. This is repeated 11 times (or more if the carbon has high gold-loading capacity). The cumulative gold loading after each contact is calculated and the data points are plotted to show the increase in the gold loading on the carbon with increasing number of solution contacts. However, the method does not appear to include a means of calculating a definitive value of the gold-loading capacity of the carbon.

2.1.3. Attrition resistance (hardness)

Attrition resistance or hardness of the carbon is (in part) inversely related to its kinetic activity. That is, increasing the internal surface area of the carbon will yield a more active material but will weaken the structure, rendering it more susceptible to breakage.

Many methods have been proposed for determining the resistance of activated carbons to particle-size degradation under service conditions, including the ball-pan hardness method, the Denver cell wet-attrition test, the stirring-bar method and the dust-elutriation method. No method has been accepted as an industry standard. However, the ball-pan hardness method has been used widely in the carbon industry and is useful for establishing a measurable characteristic of the carbon for comparison purposes.

2.1.3.1. Ball-pan hardness. Based on an ASTM method (ASTM D3802-79, 1999), this is a dry method that measures the impact resistance of the carbon. Activated carbons used in the gold industry generally have a ball-pan hardness greater than 97%.

2.1.3.2. Wet-attrition resistance. There are several methods available for the measurement of wet attrition resistance (Shipman, 1994; Avraamides, 1989;

Norit, 1992). All are based on the same principle, involving the rapid agitation of carbon suspended in water. The method can be varied by replacing the water with a pulp, typically 40% by mass (Avraamides, 1989).

2.1.4. Particle-size distribution

Methods used in the gold-mining industry are typically based on the ASTM procedure (ASTM D2862-82, 1982).

2.1.5. Apparent density

Methods used are typically based on the ASTM procedure (ASTM D2854-96, 2004).

2.1.6. Surface-area determination

Three methods of surface-area determination are of relevance to gold processing:

2.1.6.1. BET technique. The specific surface area of the carbon is measured by the adsorption of a gas of known dimension (typically nitrogen) under standard conditions of temperature and pressure, in the low-pressure range of an adsorption isotherm.

2.1.6.2. Iodine number. The iodine number represents an approximation of the surface area available to most adsorbates (Faulkner *et al*., 1987). The value is of limited use in a gold-processing plant situation but it may help in interpreting other test results (Shipman, 1994). Two methods are most commonly used for the determination of iodine number – a multiple-point ASTM Standard Method (ASTM D4607-94, 1999) and a simpler single-point procedure (Sutcliffe Speakman Carbons Ltd.; Shipman, 1994).

2.1.6.3. Carbon-tetrachloride activity. The carbon-tetrachloride activity (CTC activity) of a carbon is a measure of the micropore volume or activation level of the material (Faulkner *et al*., 1987), and is based on an ASTM method (ASTM D3467-76, 1976). This is a method that is losing favour owing to the health and safety issues associated with carbon tetrachloride.

2.1.7. Ash content

Methods used are typically based on the ASTM procedure (ASTM D2866-76, 1976).

2.1.8. Moisture content

Methods used are typically based on the ASTM procedure (ASTM D2867-76, 1976).

2.1.9. Platelet content

This test is only necessary for virgin carbons intended for use on plants using slotted screens (Shipman, 1994). The platelet content is determined by passing the carbon over a shape sorter (McArthur *et al.*, 1987) or by hand-screening over a slotted screen (Anglo American Research Laboratories Ltd).

3. MODELLING CARBON-IN-PULP CIRCUITS

Models can be useful tools for assessing the influence of design, operational variables and cost factors on circuit performance. In CIP and CIL plants, the number of these variables and the complexity of their inter-relations are such that simulation techniques can be a cost-effective means for assessing design parameters or carbon-management options (Woollacott *et al.*, 1990).

High-quality experimental data are required in order to make effective use of models and simulations (Stange, 1999). These data allow the model to be calibrated for the particular flowsheet and ore. Data may be generated from laboratory tests, or from plant performance data. Some of the design parameters that need to be considered include:

- leach feed-grade – solids and solution;
- leach-feed pulp density;
- solids flowrate;
- specific gravity (SG) of solids and solution;
- volumes of the leach and adsorption tanks, pulp density, carbon concentration;
- leach/adsorption tank profiles – gold concentration in solid, liquid, carbon;
- tailings grade and density; and
- barren and loaded carbon grades.

Modelling the CIP/CIL process has been attempted by a number of researchers since the 1980s (Dixon *et al.*, 1978; Fleming *et al.*, 1980; Nicol *et al.*, 1984a, 1984b; La Brooy *et al.*, 1986; Johns, 1986; Fuerstenau *et al.*, 1987; Woollacott *et al.*, 1990; Le Roux *et al.*, 1991; Ahmed *et al.*, 1992; Van Deventer and Ross, 1991; Jongpaiboonkit, 2003; Rees and van Deventer, 2001; Coetzee, 2003). For simplicity early models tended to be steady-state models, and did not attempt to take into account such variables as the variation in carbon particle-size or gold concentration on carbon. More recently, with improved computational capacity, population-balance techniques have been used to attempt to take these factors into account.

It is not intended to exhaustively review all the models that have been published over the years; as an overview, several of the models will be briefly described, including the Nicol model based on simple film-diffusion theory, the Stange model based on population balance and the Liebenberg and Van Deventer model based on pore diffusion.

3.1. Nicol and Fleming model

Nicol *et al.* (1984a) developed one of the first CIP/CIL process models. The model assumes that the flow of pulp and carbon are counter-current but continuous and steady-state conditions are achieved such that the concentration of gold in solution remains constant at each stage of the circuit. All tanks are assumed to be perfectly mixed. Periodic transfer of carbon is also simulated by supposing that the transfer time is very small compared to the time that the carbon remains in each tank. Results were found to be reasonable when compared to CIP pilot-plant data.

The model was tested in steady-state continuous tests and batch tests and was then extended to simulate a five-stage CIP pilot plant. The Mintek leaching kinetic model was incorporated so that the model could also be used for modelling CIL plants. The Mintek model has been further developed into a simulator that is part of the collaborative research project, AMIRA P420B; the model (SIMCIL) is accessible to sponsors of the project.

3.2. Stange model

In a series of three papers, Woollacott *et al.* (1990) presented a dynamic model of the CIP/CIL process using population-balance techniques. This model takes into account the initial gold loading on carbon particles in each stage, allowing for a distribution of gold loadings on the carbon particles in each tank and hence a distribution of adsorption rates.

This distribution takes into account the non-instantaneous nature of carbon transfer and any carbon leakage from tank to tank. The approach removes one of the major assumptions of other models, viz. that carbon transfer is instantaneous.

Stange *et al.* (1990a) used a linear kinetic adsorption rate from the Dixon model (Dixon *et al.*, 1978) in their CIP model. As this rate is linear with respect to gold loading onto the activated carbon, the weighted rate of gold loading onto the carbon is equivalent to the average gold loading. If the kinetic adsorption rate is not linear, then it is necessary to know the distribution of the gold loading to calculate the mean gold loading. This assumption of linearity removes the need to determine the loading distribution on the carbon.

The model was tested through validation testing and three case-study tests. Testing was performed for different scenarios such as carbon leakage and concurrent leaching. Model results were in quite good agreement with actual plant data.

The three case studies were performed to study the effects of carbon transfer, leaching and eluted-carbon loadings, and to demonstrate the model's ability to simulate a wide range of operating conditions. For example, for the effect of carbon transfer, four different modes of carbon transfers were modelled – carousel operation where all the carbon is transferred to the next tank, continuous-transfer operation and two types of sequential transfer.

Carrier *et al.* (1987) produced a similar model to the Stange model, also based on the Dixon adsorption rate. The model was developed by performing a differential mass-balance of gold adsorbed onto activated carbon and used the Dixon adsorption rate, without taking into account the loading distributions of the carbon particles.

3.3. Liebenberg and van Deventer

Liebenberg and van Deventer (1998) developed a CIP model that incorporated film and intra-particle diffusion, simultaneous leaching, loading of multicomponent species, and the effect of fouling and changing cyanide levels. The model is based on the branched pore model, where adsorption is described by diffusion through a liquid film surrounding the carbon particles, surface diffusion inside the pore structure of the carbon, and diffusion from the carbon macropores to the micropores.

This more recent model attempts to take into account changes in the parameters of the isotherm between tanks with an empirical relationship to the effect of changing cyanide levels down the cascade with feed cyanide concentration and feed pH as the parameters.

4. CIRCUIT DESIGN AND CARBON MANAGEMENT CONSIDERATIONS

4.1. Number of adsorption stages

Recent developments in gold processing have seen a greater proportion of circuits with a CIL, or part CIL configuration, compared to the early CIP plants. The number of leach and adsorption stages in modern CIP/CIL plants is quite variable. Fig. 1 summarizes data collected during the AMIRA P420A survey of Australasian sites undertaken in 1998–1999 (Barbetti *et al.*, 2000).

Most of the sites have none or only one or two leach tanks. As the number of adsorption stages increases, the amount of carbon required at each stage decreases (Stange, 1999). Consequently, the total amount of gold locked up

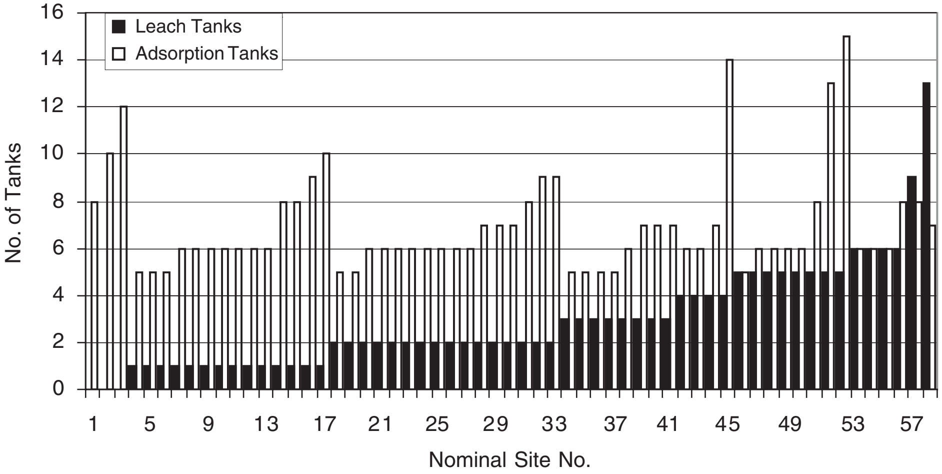

Fig. 1. Number of leach and adsorption tanks for Australasian operations (after Barbetti *et al.*, 2000).

in adsorption and total carbon inventory also decrease. The number of stages also influence the loss of gold from the circuit on abraded carbon since the rate of carbon abrasion decreases as the total amount of carbon in the adsorption circuit decreases. This effect diminishes with increasing number of stages so that a point is reached (*i.e.* 8–10 stages), where insignificant benefits are obtained from increasing the number of stages further. At this point, the capital and operating savings obtained are outweighed by the incremental capital required to install more adsorption tanks.

In summary, increasing the number of stages will have the following effects on the circuit (Bailey, 1987):

- less carbon is required to achieve the same barren solution gold concentration;
- higher gold loadings on the carbon in each stage (except the first stage);
- lower weighted-average gold loading on carbon;
- less gold lock-up (lower gold inventory);
- less carbon abrasion and gold loss; and
- shorter carbon retention time, thus lowering fouling potential.

CIL can often be an attractive option. There are advantages from a capital cost point of view but this arrangement may present a number of operational problems. For example, carbon and gold inventory is higher for a CIL operation compared to a typical CIP operation (Nicol *et al.*, 1984b). As a consequence of the greater carbon inventory, CIL plants experience increased carbon breakage, representing increased loss of carbon and gold. There is also a greater risk of carbon fouling. Stange *et al.* (1990b) also note two other beneficial effects resulting from the separation of the leaching and adsorption circuits:

(1) The overall extraction of gold from the ore is increased owing to increased residence time in the leach.
(2) The increase in solution tenor in the adsorption feed, combined with the fact that little leaching takes place in the last few stages in the plant, results in improved adsorption performance and overall increase in gold recovery.

The difference between the CIL and CIP routes is reduced as more stages are added and the required inventory is decreased (Bailey, 1987). The extra gold and carbon inventory associated with CIL will reduce the capital cost difference between the two routes.

The amount of carbon in the CIL circuit is not dependent on the size of the vessels but on total gold input and number of stages. A typical CIL circuit will have lower carbon concentrations than in a CIP circuit because the leach vessels are typically much larger than normal adsorption vessels. The amount of pulp that has to be transferred to move the required amount of carbon is therefore significantly increased. This increases the flow through the interstage screens, which have either to be enlarged or supplemented by external screens. Transfer times tend to be longer than for CIP operations and the plant is upset for longer periods. In addition, leaching and adsorption requirements may easily be in conflict and optimization of these stages may be difficult to achieve.

Nicol *et al.* (1984b) applied their CIP model to a typical CIL application comprising eight stages with a pulp residence time of 3 h per stage. Situations were investigated in which carbon was present in all the stages or only the last 7, 6, 5 or 4 stages of leaching, *i.e.* with a varying number of pre-leaching stages. To achieve the same performance and optimum carbon and gold inventory, two stages of leaching only (pre-leaching) prior to carbon addition were found to be optimum. This will vary with head grade and desired tailings grade but only in very exceptional cases should more than 5–6 h of pre-leaching be required. In cases where the head grade or the desired gold concentration in the barren solution is higher, one or no pre-leaching stages (*i.e.* carbon is added to all stages) would be required.

4.2. Pump cells and carousel circuits

One of the few significant mechanical innovations in CIP in the last 15 years has been the introduction of the AAC pump cell produced by Kemix

Pty Ltd (Whyte *et al.*, 1989; Rogans and Cartner, 1996). The pump cell combines pumping, screening and agitation in a single-drive unit with a high rate agitation. The design permits high carbon densities, resulting in short residence times for the pulp. As a result pump-cell dimensions are much smaller than typical carbon-adsorption stages in CIP or CIL operations. A list of currently installed pump-cell plants is given in Table 2.

The Pump cell is particularly applicable to a carousel adsorption-circuit configuration. In the carousel system, each batch of carbon spends the entire adsorption cycle in one tank. Instead of transferring carbon, as is done in normal CIP operations (sometimes called cascade CIP), the feed and discharge points of each contactor are changed sequentially. Advantages of the carousel system include:

- elimination of carbon back-mixing due to carbon not being transferred as a batch in cascade CIP;
- removal of the recirculating-pulp load;

Table 2
Pump-cell installations (after Kemix, 2004)

Location	Date installed	Cell size (m^3)
Vaal Reefs, South Africa	Sep 01	70
Vaal Reefs, South Africa	Mar 92	70
Hartebeestfontein, South African	Dec 93	100
Vaal Reefs, South Africa	Mar 94	70
El Indio, Chile	Feb 94	70
JCI-Cons Murch, South Africa	May 95	35
Driefontein No.3, South Africa	Dec 95	80
Blyvooruitzicht, South Africa	Nov 96	100
Pharoah, Australia	Jan 97	12
Western Deeps Level, South Africa	Apr 98	110
Elandsrand, South Africa	Aug 98	90
Driefontein No. 2, South Africa	Sep 00	100
Kloof No. 1, South Africa	Sep 00	90
Driefontein No.1, South Africa	Dec 00	125
South Deep, South Africa	Mar 01	200
ERPM, South Africa	Jan 02	40
Kloof No. 3, South Africa	Nov 02	70
Barbrook, South Africa	Dec 02	–
Amantaytau, Uzbekistan	Mar 03	70
Blyvooruitzicht, South Africa	Jun 03	100
Glamis, Mexico	Aug 03	70
St Ives Gold Mine, Australia	Late 04	–

- reduced capital costs; and
- reduced operating costs.

Rogans and McArthur (2002) compared the performance of two pump-cell circuits with a standard adsorption circuit at Anglogold's West Wits operations. The pump-cell circuits were operated by moving all the carbon in a contactor every 2 days, with carbon concentrations of 25–50 g/L. Typical upgrade ratios (ratio of gold on loaded carbon to gold in feed at operating equilibrium) was found to be 800–1,000 for the cascade CIP circuit and 1,800–2,000 for the pump-cell circuits. Soluble losses were found to be lower for the pump-cell circuits, with gold lock-up being similar or slightly higher to the conventional circuit. Significant cost savings were achieved in elution with the pump-cell circuits due to the higher gold loadings.

4.3. Carbon residence time

An important consideration related to carbon residence time is that the longer the carbon remains in contact with the pulp, the greater the extent of fouling and the greater the detrimental effect on adsorption of gold (Stange, 1999). Total carbon contact time will be influenced by the number of stages, the amount of carbon in each stage, the mode of carbon transfer and the total rate at which carbon is moved. Higher carbon residence times usually reflect larger carbon inventories (and lower carbon activity).

Fig. 2 summarizes the calculated residence times for carbon from the various Australasian operations evaluated in the AMIRA P420A industry survey (Barbetti *et al.*, 2000).

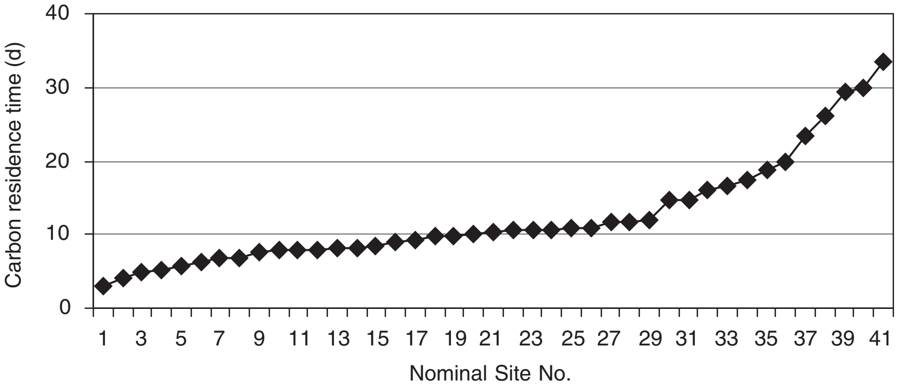

Fig. 2. Carbon residence times in Australasian operations (after Barbetti *et al.*, 2000).

Table 3
Impact of carbon activity on solution tail

Carbon activity kK	% relative to base case	k	K	Solution tail (mg/L)	Change in solution tail (%)
130.075	110	0.011	11,825	0.006	−14.3
130.075	110	0.0121	10,750	0.006	−14.3
118.25	**100**	**0.011**	**10,750**	**0.007**	**0.0**
106.425	90	0.011	9,675	0.009	28.6
106.425	90	0.0099	10,750	0.008	14.3
94.6	80	0.011	8,600	0.014	100.0
94.6	80	0.0088	10,750	0.009	28.6

4.4. Effect of carbon activity on soluble gold loss and carbon inventory

A higher carbon inventory is often the result of a low carbon activity, caused either by inefficient regeneration or circuits with high fouling capacity, *e.g.* flotation tails circuits.

Table 3 is a summary of a study of the impact of carbon activity on solution tail loss. Actual plant data (in bold) was modelled using SIMCIL (Parker Centre, 2004). The *activity* of the carbon (defined as the product of k (activity constant) and K (equilibrium loading constant)) was then varied, and the change in solution tail loss calculated. The results show that relatively small changes in carbon activity can dramatically affect solution losses of gold.

Fig. 3 summarizes the effect of carbon activity on carbon inventory, based on plant data, where plant carbon inventory was 140 t and solution loss 0.017 mg/L Au.

Stange (1999) suggested that it is not unreasonable to expect gold tenors in solution in adsorption tails to be less than 0.005 mg/L. This value will more easily be achieved in cases where:

- there is sufficient carbon in the adsorption plant;
- good eluted-carbon assays (<40 g/t) are routinely achieved;
- there is a minimum of leaching in the last few adsorption stages;
- carbon activity is consistently high through good acid washing and
- regeneration practices; and
- there is minimal co-current flow of carbon through the circuit caused by leakage of carbon through interstage screens.

The final point is of particular importance for slotted screens. Off-specification or poorly prepared carbon may contain a large fraction of granules that are of a shape or size that can pass through the screen. Leakage also results from

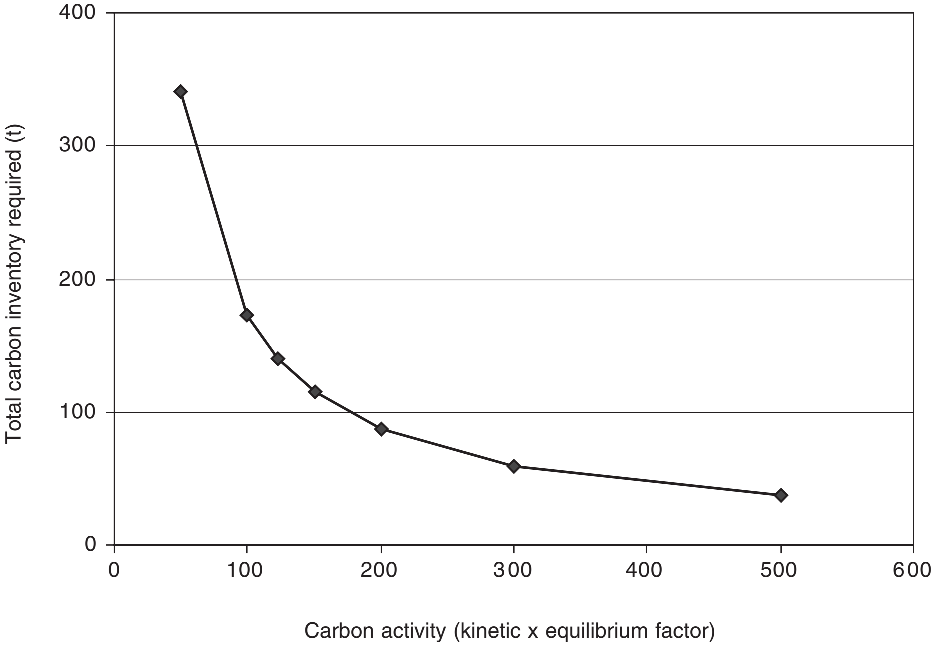

Fig. 3. Impact of carbon activity on carbon inventory.

holed screens due to poor maintenance. Relatively little concurrent flow of carbon is required for the efficiency of adsorption to be affected adversely (Stange *et al.*, 1990a). Whyte *et al.* (1989) reported the results of a simulation exercise in which it was found that a concentration of only 0.06 g/L carbon in the interstage slurry led to an increase of 21% in the average barren solution value and a 24% increase in the gold lock-up.

4.5. Effect of carbon distribution on soluble gold loss

It has often been suggested that more carbon should be added to the later stages of an adsorption circuit than to the early stages to scavenge gold (Nicol *et al.*, 1984b). In theory, this will result in more effective operation with reduced concentrations of gold in the barren solution. The Nicol/Fleming model showed that if carbon is distributed uniformly throughout the plant, each stage extracts the same fraction of gold from solution as that which enters the stage. A greater fraction in either the first or last two contactors results in a higher concentration of gold in the barren solution, *i.e.* the minimum carbon inventory is realized when the carbon is distributed uniformly throughout the adsorption circuit. Bailey (1987) noted, however, that the gold lock-up is lower if more carbon is held in the latter stages, and this may provide economic grounds for a skewed carbon distribution.

Stange *et al.* (1990b) reported on the simulation of a six-stage CIL circuit. It was found to be highly advantageous to distribute the carbon so that the stages at the pulp effluent end of the cascade contained more carbon than the stages at the feed end. For this situation, 27% less carbon was required to produce the same tailings grade as the evenly distributed case. In addition, the gold lock-up was 40% lower.

Modelling Australasian circuits using SIMCIL has generally shown little or no benefit by skewing carbon distribution to either the front or back of the circuit. Two exceptions to this general rule are (i) where leaching continues down the circuit, there is an advantage is moving the carbon to the back of the circuit; and (ii) where the ore contains a *preg-robbing* component, advantage can be gained by having higher concentrations of carbon in the front of the circuit. One significant factor that has been noted in the modelling is the effect of variable carbon distribution in a circuit on soluble gold loss (see Table 4). This occurs when carbon transfer is intermittent, limited by equipment, or the result of overflow of inter-stage screens.

It can be seen from the table that, after normalizing the carbon inventory, the minimum solution-loss result is achieved with equal concentration of carbon in all tanks. Significant additional solution loss results with variable distribution. The model successfully predicted the trend observed in the plant.

4.6. Effect of barren-carbon grade on soluble gold loss

Barren-carbon grades of 20–50 g/t Au should be readily achievable following elution. Results from the AMIRA P420A industry survey (Barbetti *et al.*, 2000) showed that barren-carbon grades in Australasian gold plants ranged from 10 to 350 g/t Au. The barren-carbon grade can have a significant effect on soluble gold loss, particularly affecting the efficiency of the final carbon-adsorption stage. Table 5 summarizes the results of a SIMCIL modelling exercise studying the effect of barren-carbon grade on an operating plant, showing that ~100 g/t gold on barren carbon can increase soluble gold loss by ~0.01 mg/L.

4.7. Carbon usage rate

Fig. 4 summarizes the carbon usage rate reported by Australasian operations as part of the AMIRA P420A industry survey (Barbetti *et al.*, 2000).

The majority of sites reported carbon losses of between 10 and 30 g carbon per tonne of ore. The rate of carbon attrition is typically a function of carbon inventory, elution rate (*i.e.* gold loading) and carbon handling during transfer, elution and regeneration.

Table 4
Impact of variable carbon distribution on solution tail

Carbon concentration description	Carbon concentration (g/L) (normalized to total inventory of 28.4 t)						Total measured inventory (t)	Predicted solution assay in last tank (mg/L)
	Tank A	Tank B	Tank C	Tank D	Tank E	Tank F		
Even	10.65	10.65	10.65	10.65	10.65	10.65	(28.4)	**0.025**
GIC 25/08/2002	6.0	4.5	6.0	25.0	14.0	8.5	35.4	**0.040**
GIC 01/09/2002	5.5	8.0	4.5	9.0	16.5	20.0	25.6	**0.036**
GIC 08/09/2002	0.5	6.5	9.0	17.0	16.0	15.5	37.9	**0.095**
GIC 15/09/2002	13.5	13.0	5.0	11.5	5.5	15.5	28.9	**0.030**
GIC 22/09/2002	10.5	8.5	7.0	16.5	11.5	10.0	25.3	**0.027**

Table 5
Effect of barren-carbon grade on soluble gold loss

Barren-Carbon Grade (g/t)	Tank 6 Carbon Loading (g/t)	Gold on Carbon (kg)	Solution Tail (mg/L)
25	64	25.7	0.021
51	**90**	**26.0**	**0.024**
100	138	26.9	0.030
150	188	27.7	0.035

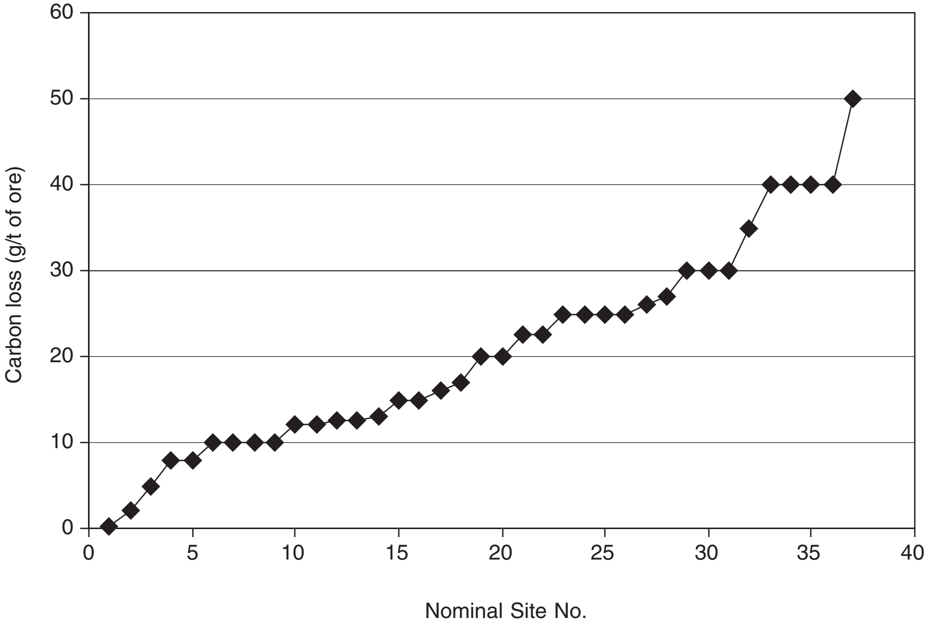

Fig. 4. Carbon usage rate for Australasian operations (after Barbetti *et al.*, 2000).

High carbon inventories result in extended carbon residence, with the carbon being subjected to increased attrition time in the tanks. However, the major source of carbon loss is during the elution and regeneration stages, arising from mechanical factors during carbon transfer (short radius bends in transfer piping, high pumping velocity, high carbon density and screening) or from uncontrolled regeneration leading to burning of the carbon, resulting in reduced attrition resistance.

4.8. Target gold loading on carbon

Higher gold loadings on carbon have the beneficial effect of decreasing the size requirements of the elution-regeneration plant. Some savings in

Table 6
Effect of carbon loading (elution rate) on solution tail

Elution rate (strips per day)	Carbon movement rate (t/h)	Modelled loaded carbon assay (g/t)	Modelled solution tail (mg/L)
0.57	0.165	3,000	0.029
0.63	0.185	2,700	0.025
0.71	0.208	2,400	0.021
0.82	**0.239**	**2,100**	**0.018**
0.96	**0.280**	**1,800**	**0.015**
1.16	0.337	1,500	0.013
1.34	0.390	1,300	0.011
1.52	0.442	1,150	0.010
1.75	0.511	1,000	0.009

carbon usage rate may also be achieved owing to reduced carbon handling. Carbon inventory will not be significantly affected, although the average carbon activity in the circuit may decrease due to longer average carbon residence times (Bailey, 1987).

Carbon loading is strongly influenced by the gold tenor in the pregnant solution. Loaded carbon values can be up to 10,000 times higher than the gold tenor in solution (Barbetti *et al.*, 2000). Fouling will limit the loading value to a significant extent.

Table 6 summarizes the results of a SIMCIL modelling study of an Australian operation showing the effect of carbon loading (elution rate) on gold soluble loss. The results reflect the practical limits on gold loading that can be achieved in operations with relatively low-grade solution tenor and low activity carbon

4.9. Gold-loading distribution

Woollacott and Erasmus (1992) described a study of the distribution of gold loadings on a loaded carbon taken from one day's production in a South African CIP operation. They suggested that the gold loading is distributed among the carbon particles for two main reasons:

(1) The smaller the particle the greater the adsorption rate. Although the size range of particles in the circuit is relatively small, it is nevertheless significant. For the same contact time, the smaller particles will become loaded to higher values than the larger particles, and the gold loadings on individual particles will be distributed as a result.
(2) The method of carbon transfer also has an effect. The mean gold loading on the carbon in the circuit decreases from the first to the last contactor in

> the adsorption train. During the transfer cycle carbons from different tanks become mixed to some degree, unless the complete carbon inventory in each tank is instantaneously moved upstream.

Stange and King (1987) simulated the effect of the amount of carbon transferred on the distribution of gold loadings in a particular CIP adsorption circuit. They suggested, as expected, that the larger the proportion of carbon moved, the smaller will be the fraction of carbon that is very highly loaded, and the narrower the distribution of gold loadings.

In the Woollacott and Erasmus study, it was found that 11% of the carbon contained 30% of the gold, this carbon being classified as small, highly loaded particles which could impair the performance of adsorption and elution processes. Such particles would have lower than expected adsorption rates before they are removed from the adsorption circuit. In addition, some fraction of the gold in these particles is likely to be found in the smaller pores of the carbon and so may be less accessible to elution. Modifying operating practices to reduce the proportion of carbon that is loaded in this way should improve the adsorption and elution.

4.10. Carbon transfer

Carbon movement can either be performed in one transfer per day or numerous small transfers using either of the following methods (Bailey, 1987):

1. Loaded carbon is transferred from the first tank and then sequentially down the bank until regenerated carbon is added to the last tank. This is known as *sequential down-bank transfer* or *pulling*.
2. Regenerated carbon is added to the last tank and then carbon is transferred sequentially upstream until loaded carbon is transferred from the head tank. This is known as *sequential up-bank transfer* or *pushing*.

Down-bank transfer temporarily depletes one stage of carbon, which creates longer transfer times, effectively reduces number of stages available for gold recovery, and results in significant loss of gold to tails. This loss increases substantially if the activity of the carbon is reduced.

Up-bank transfer temporarily doubles the carbon concentration in one of the stages, returning to normal as the batch is transferred. This transfer regime creates more mixing of the carbon and a flatter gold on carbon profile but is considered more desirable than increasing tails loss. Hence, up-bank transfer is the preferred method.

The relative performance values for the transfer of various fractions of the carbon inventory at each stage during each cycle are given in Table 7 (Nicol *et al.*, 1984b). These values are for an ideal case and do not allow for effects

Table 7
Relative performance for the transfer of various fractions of the total carbon inventory (after Nicol et al., 1984b)

Fraction transferred per cycle	Relative performance (%)
1.00	100
0.50	95
0.25	92
0.10	90
Continuous	88

such as carbon fouling. It can be seen from these values that one single transfer is more efficient than frequent small transfers.

The operating costs associated with elution and regeneration are proportional to the rate of carbon transfer through the circuit (Fleming, 1983). Optimum carbon flowrate must be balanced against the return that could be expected from investment of the value of the gold and carbon locked up in the plant.

5. CONCLUSIONS

This chapter has focused on advances made in the design and operation of CIP and CIL plants. Most of the advances over the last 10 years or so have been in the area of carbon management. Trends towards cyanide-free elution (*e.g.* Adams, 1995) are becoming more prevalent, impacting positively on operating costs. While the elution and regeneration components are essential aspects of a CIP plant, in practice, the capital cost of this area of the plant is a relatively small part of the overall project cost and can therefore be engineered with a higher contingency factor (see Chapter 6 for a more detailed discussion).

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Chapter 24

Zinc cementation

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1. INTRODUCTION

The use of zinc, either in the form of dust or shavings, has been a well-known part of the Merrill–Crowe process, incorporating zinc cementation for the recovery of gold and silver from pregnant solutions, since 1888. The process is a classic cementation reaction involving oxidation and reduction. Normally applied to solutions generated either from a solid–liquid separation step downstream of a grinding and leaching operation, or from solutions originating from heap-leaching, it has also been used on eluates from carbon stripping and solutions from intensive cyanidation. The expensive solid–liquid separation step following grinding operations, which is required for the Merrill–Crowe process can now largely be avoided by the use of the carbon-in-pulp (CIP) process. However, the zinc cementation process still accounts for some 25–30% of world gold production (Marsden and House, 1992). It has also retained certain specific specialist metallurgical applications: when the silver-to-gold ratio in solution is high, or when the mercury content of the pregnant solution is high, or when high concentrations of flotation reagents or other organics are present, or when the scale of operation is small.

2. CHEMISTRY

Cementation is an electrochemical, precipitation reaction involving oxidation and reduction processes, sometimes referred to as a *redox* reaction.

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The reaction describing zinc cementation of gold is given as follows:

$$2\mathrm{Au(CN)}_2^- + \mathrm{Zn}^\circ \rightarrow 2\mathrm{Au}^\circ + \mathrm{Zn(CN)}_4^{2-} \quad (1)$$

An alternative reaction (Marsden and House, 1992), thought to be more representative of actual conditions and stoichiometry, is shown as:

$$\mathrm{Au(CN)}_2^- + \mathrm{Zn}^\circ + 4\mathrm{CN}^- \rightarrow \mathrm{Au}^\circ + 2\mathrm{CN}^- + \mathrm{Zn(CN)}_4^{2-} \quad (2)$$

The gold atom accepts one electron and is reduced from the (+1) oxidation state to the metallic (0) oxidation state; the zinc atom donates two electrons and is oxidized from the metallic (0) state to the (+2) oxidation state. Gold metal coats onto the zinc particle, which continues to corrode and dissolve.

The electromotive series is a list of metals, whose order indicates their relative tendency to be oxidized or donate electrons. It begins with those metals most easily oxidized (Li, K, Ca, etc.) and ends with those most difficult to oxidize (Hg, Ag, Pt and Au). The order corresponds to an increasing oxidation potential, expressed in volts, and is a measure of how readily oxidation will take place. It is sometimes called the replacement series in that any metal with a lower oxidation potential will replace a metal in a chemical compound with a higher oxidation potential in the way that zinc (−0.76 V) replaces gold (+1.5 V).

It is interesting to note that lead has an intermediate oxidation potential (−0.126 V). Various texts refer to the soluble lead salt forming a *lead–zinc couple* during this reaction, a description of its role as a catalyst. The soluble lead salt can be added as either lead acetate, or more commonly, lead nitrate.

As with most cyanidation reactions, the pH value should be maintained above 10.5 to inhibit the evolution of HCN gas. The optimum free-cyanide concentration corresponds with the typical residual level present after cyanidation leaching of 150–200 mg/L, expressed as NaCN. Lower cyanide levels favour zinc hydroxide formation, which passivates or inhibits the reaction; higher levels can dissolve the metallic zinc, thus increasing zinc consumption. If excess zinc is added, zinc hydroxide formation is favoured.

Although temperature increases the rate of reaction, the reaction is very fast even at low temperatures just above freezing. High temperature and increasing altitude reduces the equilibrium oxygen content of solutions. Dissolved-oxygen levels of less than 1 ppm are optimum for the reaction; higher values reduce reaction kinetics because oxygen reduction competes with gold reduction. The presence of oxygen can also promote re-dissolution of gold by cyanide.

Soluble sulfides at less than 20 mg/L can be very detrimental to precipitation, owing to the formation of an insoluble zinc-sulfide layer. Early operators noticed that the presence of small amounts of trapped sulfide particles in boxes containing zinc shavings lowered zinc consumption. This was attributed to the fact that these sulfides reacted with cyanide and oxygen and reduced the oxygen content of the solution.

In practice, gold, silver and mercury are precipitated with high efficiencies, in excess of 99.5%. Some base metals, notably iron and some copper, nickel and cobalt are precipitated but at a much lower efficiencies. Copper pre cipitation can be inhibited by increasing the cyanide concentration; higher cyanide concentrations may be necessary to initiate effective gold precipitation in the presence of high-copper levels.

3. HISTORY

The use of the zinc cementation process for gold recovery was first patented in Great Britain by J. MacArthur and Drs. R. and W. Forrest in 1888. Initial applications were at the Crown mine in New Zealand and Robinson Deep in South Africa during the 2 years following patenting. It soon became the preferred gold recovery step and an integral part of the cyanidation process. The first application in the USA was by C.W. Merrill at the Homestake mine in Lead, South Dakota.

Zinc cementation was initially performed in sloping boxes filled with bundles of coarse zinc shavings. Gold-bearing solutions were passed through sand filters ahead of this step to remove suspended solids. However, the coarse zinc shavings became coated, and essentially passivated with insoluble zinc hydroxides, so zinc consumption was high. To alleviate this effect, three main improvements to the process were made (Marsden and House, 1992; Hampton, 2002):

- The first improvement was the use of a lead salt; this was achieved by dipping the bundles of zinc shavings in lead acetate.
- The second was the substitution of zinc powder in place of the zinc shavings (C.W. Merrill).
- The third was the introduction of de-aeration through the use of a vacuum de-aeration tower (T.B. Crowe).

These three improvements were initiated in the 20 years following the initial patenting and introduction of the process; since then, the main improvements to the Merrill–Crowe process have been equipment related. Ongoing refinements, such as the introduction of Stellar filters, have simplified operation, reduced operating costs and increased the size of plants. The use of the basic process has been expanded to include gold recovery from carbon-stripping eluates and solutions originating from intensive cyanidation.

4. APPLICATION

The alternative processes, CIP or carbon-in-leach (CIL), have become the preferred process route over the Merrill–Crowe process for medium and large-scale gold processing plants since the late 1970s, owing to their lower capital and operating costs (see Chapter 23). These lower costs are mainly due to the non-requirement of the solid–liquid separation step inherent with the Merrill–Crowe process. Except in the case of heap-leaching, this step typically involves two-stage rotary-drum filtration or up to six stages of counter-current decantation thickeners. The solid–liquid separation step is necessary to separate the gold-bearing solution from the leached solid residue. In the carbon-based processes, the gold is adsorbed onto carbon granules during or following cyanide leaching. They can then be easily screened and washed from the leach slurries. However, despite these potentially higher capital and operating costs, the Merrill–Crowe process still finds application for certain specific applications.

4.1. High silver/gold ratio

Merrill–Crowe is preferred over carbon-based processes when the silver/gold ratio in the leach solution is high. A number of papers address this subject, which is covered in more detail in Chapter 34, but consideration would be given to Merrill–Crowe process when this ratio exceeds 2 or 3. Under typical plant operating conditions, the presence of cyanide-soluble silver lowers the maximum gold loading of the activated carbon. This means that for a given concentration of gold in solution a higher amount of carbon must be moved through the leach tanks and screened out for subsequent stripping. This increases the capital and operating costs for the carbon-based processes and can result in the Merrill–Crowe process being selected for economic reasons.

4.2. High mercury content

In both heap-leaching and agitated-tank leaching operations, mercury can be dissolved from the ore by cyanide. In plants using the carbon-based processes, soluble mercury–cyanide complexes are adsorbed onto the activated-carbon granules. The mercury is later removed during the elution process step along with the gold and silver. However, it can contaminate working areas during the various processing steps after elution, i.e., pregnant and barren strip-solution storage tanks, carbon-regeneration kiln and electrowinning cells.

The cathodes can be retorted to recover residual mercury, but by that point in the process, significant mercury losses and contamination can have occurred.

These losses and subsequent contamination are more controllable when the Merrill–Crowe process is used. The mercuric–cyanide complex is removed at $>95\%$ efficiency from clarified solution by zinc cementation. The precipitated mercury is recovered along with the gold and silver in the filtration step, immediately following precipitation. The precipitate is collected from the filter and transported directly to the retort furnace. The improved mercury management that is associated with the Merrill–Crowe process can lead to the selection of this process route over carbon in solution. This is particularly true for heap-leaching operations, where the Merrill–Crowe process or the alternative carbon-based gold recovery step from solution have similar capital costs, but the operating cost associated with carbon stripping can be higher than for Merrill–Crowe.

4.3. Other applications

Merrill–Crowe is less affected by flotation reagents and other organics than a carbon-based process and could be considered as an alternative when flotation concentrates are being leached. The activated-carbon granules adsorb the reagents and other organics and this can affect their gold-loading capability by tying up available sites. Costs for smaller, higher-grade plants using the Merrill–Crowe process can sometimes be lower than for plants using a carbon-based process, owing to the relatively high capital and operating costs of the carbon-stripping plant.

5. BASIC FLOWSHEET

The basic Merrill–Crowe flowsheet is shown in Fig. 1.

The main steps in the Merrill–Crowe process are: clarification, de-aeration, zinc cementation and filtration. Solution is received either from the pregnant-solution pond of a heap-leach operation or from the unclarified solution tank of a solid–liquid separation section. The solution must be clarified to around 1 ppm suspended solids for effective cementation to occur. After clarification, the solution is pumped from the clarified-solution tank to the de-aeration or Crowe tower. A vacuum is applied to this tower and the dissolved-oxygen content of the solution is lowered from around 7 ppm to below 1 ppm. The solution flows out of the tower to the filter-press feed pump. A stream of barren solution containing the zinc powder enters the piping ahead of the pump suction from the zinc cone or emulsifier. Lead nitrate may also be added at this point if required. The precipitated, or cemented gold and other precious metals, as well as excess zinc and other base metals are collected in the precipitate filter. Periodically, this filter is emptied. The precipitate may

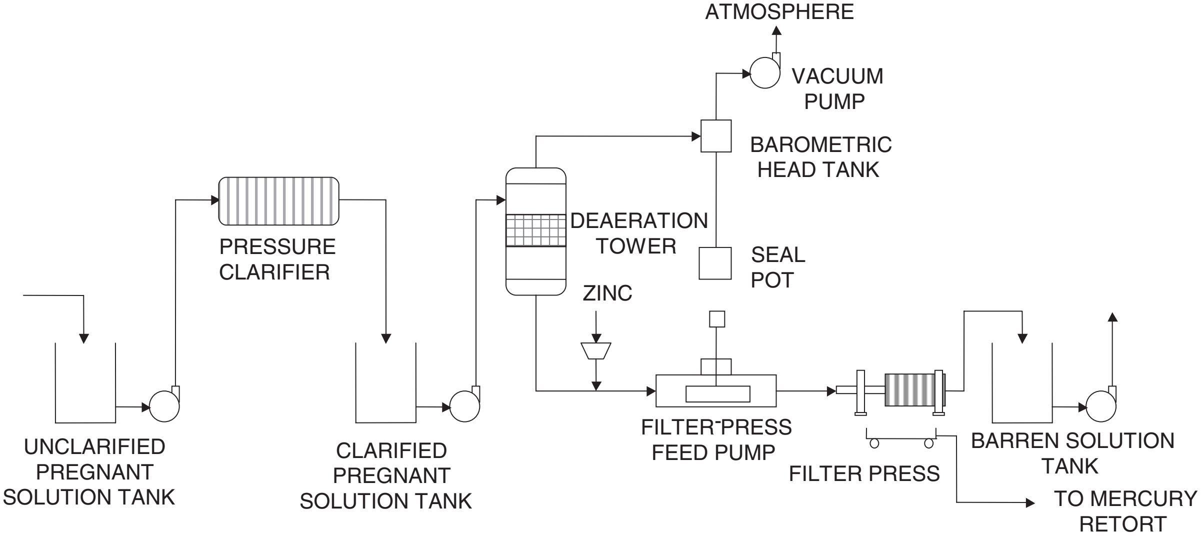

Fig. 1. Merrill–Crowe flowsheet.

be retorted, dried or calcined ahead of refining, depending on its mercury and base-metal content.

6. EQUIPMENT

6.1. Clarification

This step can involve one or two stages depending on the clarity of the incoming solution. The first stage, if employed, is typically a rake clarifier or a hopper clarifier. This step improves the clarity of the solution to less than approximately 25 ppm suspended solids. The second step is typically a pressure leaf-filter or sand clarifier. The leaf-filter is better suited to produce the required clarity of ~1 ppm suspended solids required for effective precipitation to occur. These types of filters have replaced the use of both the vacuum leaf-filter and filter press, which were used earlier in the 20th century. The use of diatomaceous earth as a pre-coated filter aid is widely used to achieve the filtration rates and clarity of solution required. As well as *pre-coat*, it is sometimes also added continuously during clarification as *body feed*.

6.2. De-aeration

De-aeration or Crowe towers can follow a number of designs. More recent designs employ packed towers or cascade or splash towers fitted with offset plates. Early designs used a variety of wooden lattices or strips. A variety of solution-distribution launders, pipes or sprays are also used. The vacuum is typically applied to the top of the tower by a liquid-ring vacuum pump using barren solution as seal water. Operators often experience loose tower packing finding its way into the vacuum pumps. This can be prevented by installing a simple retaining grid. The tower should also include a vortex breaker at the solution outlet.

Some plants include a barometric head tank located between the tower and the vacuum pump. This tank, with its associated barometric leg, prevents the possible carryover of gold-bearing solution to the vacuum pump, particularly during flooded conditions. It also acts as a vacuum receiver in the same way as an air receiver on a compressed-air system. The barometric leg typically sits in a solution-filled seal pot, which provides a vacuum seal.

Once the solution has been de-aerated, it is imperative that air ingress to the solution be prevented. Welded pipe is recommended between the deaerator and the filter press, and the pump suctions must be adequately designed or protected. The filter-press feed pump can be one of many designs, including vertical and horizontal centrifugal. A vertical in-line pump submerged in a bath has been found to be effective in excluding air, and hence oxygen, entering the de-aerated solution. However, horizontal centrifugal pumps with either packed glands or mechanical seals have also been successfully applied. Care must be taken to review the tower operating level to provide the required net positive suction head for the filter-press feed pumps and avoid cavitation. Sufficient residence time in the lower portion of the tower should also be provided to allow the level-control system to function effectively. Although instrumentation sensors and control valves are now typically used to control tower level, earlier designs used an overflow pipe, located below the packing, which returned solution from the tower to a small vacuum-seal tank located in the clarified-solution tank.

6.3. Zinc cementation

This step can occur in a zinc cone or emulsifier that can be in line with the main process-solution flow, i.e., located under the de-aeration tower or alternatively located above the suction line of the filter-press feed pump, as shown in the flow diagram. Experience has shown that most precipitation actually occurs in the precipitate filter as the solution passes through the cake of precipitate, which contains excess zinc, rather than at the point of zinc addition. Early zinc feeders were slowly moving conveyor belts, which tended to add zinc in small batches as it fell off the end of the conveyor. A new generation of controllable vibrating or pulsed feeders are now available. The improved control has led to reduced overall zinc consumption and more reliable precipitation. Although zinc is typically added dry, some operations premix it with a cyanide solution. This can return any zinc oxides and hydroxides present back to the metallic state.

A bleed from solutions circulating in a Merrill–Crowe plant is often required to control the build-up of zinc, iron and other base-metal cyanide concentrations. The treatment of this bleed stream in a cyanide-destruction plant should be considered during design.

6.4. Precipitate filtration

The plate and frame, or recessed-plate filter press is widely used to recover the precipitate. Although labour-intensive to empty and put back on line, it is relatively inexpensive to install. Recent improvements on the larger filter presses now available include plate shifters to progressively move the plates forward to facilitate emptying. The use of filter cloths or papers between the plates can make cake release and press cleaning easier. The main alternative equipment is a candle filter. These units have the advantage of being easy to automate and backwash. A disadvantage is that the backwashed precipitate is a dilute slurry and a second filtration step, such as a pre-coat rotary drum filter, is required. A recently proposed variation involves a polishing leaf-filter to initially recover the precipitate. The precipitate is then backwashed and recovered in a pressure filter similar to those used to dewater flotation concentrates. This has the advantage of being able to dry the precipitate to low moisture contents, reducing the load on downstream drying, calcining or retorting equipment. Other advantages are associated with security and materials handling.

6.5. Precipitate handling and treatment

On some of the larger plants, precipitate volumes can be large and consideration must be given to facilitating material handling, particularly in the case of filter presses. Relatively simple conveyors, roller conveyors or trolleys and even storage bins can be employed to transport the precipitate to drying ovens, retorts or refining furnaces. Also, hygiene and dust control are important as the precipitates can contain mercury. In certain operations, precipitates can have a high base-metal content and a sulfuric, hydrochloric or nitric acid digestion step is employed to dissolve iron, copper and other base metals. If possible, this should be avoided, as the handling of the acids themselves, as well as the handling of the viscous acidic base-metal solutions produced is difficult and potentially dangerous, due to the evolution of hydrogen gas. However, recent advances in polymeric or fibreglass materials make design and specification of this equipment easier. If the precipitates contain mercury, then a mercury retort will be required; otherwise drying or calcining in a tray oven is employed. Calcining refers to oxidation of the base metals in the precipitate so that they report to the slag during refining. When correctly done and combined with an effective flux, this step can eliminate the requirement for acid digestion.

7. DESIGN CRITERIA

The Merrill–Crowe zinc-cementation process has been applied on a wide range of metallurgical applications. Table 1 gives typical values, or ranges, for the main design criteria.

Table 1
Typical design criteria for Merrill–Crowe plants

	Typical Value or range	Comments
Pregnant solution grades	Up to 5 mg/L Au	Grades are obviously variable; heap-leach solutions are typically around 1 mg/L gold while solutions from a mill may be higher
	Up to 100 mg/L Ag Up to 5 mg/L Hg	High mercury values of up to 50 mg/L can affect filtration of the resultant precipitate

Table 1 (*continued*)

	Typical Value or range	Comments
Clarification filtration rates	2.5–3.0 $m^3/h/m^2$	Typical values for a pre-coated, pressure leaf-filter operating with *body feed*
De-aeration tower	Large towers can be sized using 130–190 $m^3/h/m^2$ (3,100–4,600 $m^3/d/m^2$.) Smaller towers typically use 70–85 $m^3/h/m^2$ ($\sim$2,000 $m^3/d/m^2$)	
De-aeration tower vacuum	3–10 kPa (absolute) is required to achieve less than 1 ppm O_2 in solution	The process will work at a less effective vacuum but provision of an effective vacuum is cost-effective over the life of an operation
De-aeration tower vacuum pump	1.4–2.4 Am^3/h of air per m^3/h of solution, or 300 Am^3/h of air per m^2 of tower area, or 15 kW/m^2 of tower area	These values are applicable at sea level and high-altitude sites
Actual zinc addition	1.0 kg zinc per kg of precious metal and mercury to be precipitated. The requirement decreases with increasing solution grades ($\sim$3 times the stoichiometric requirements)	Higher consumption values are quoted in South African operations. Higher doses are often used during start-up of a filter
Lead nitrate addition	0–0.2 kg/kg zinc or up to 15 g/m^3	
Precipitation filtration rates	1.5–3.0 $m^3/h/m^2$	Typical values for a pre-coated filter press
Precipitate grades	20–80% Au and Ag; 50% is often used for design purposes; 5–30% Zn Insoluble oxides, sulfates and carbonates – 5–15%	A wide range of values is quoted. This value can be raised in heap-leach operations by turning off zinc addition prior to press cleanup. This consumes any unused zinc in the cake residing in the filter press
Precipitate moisture	50% is used for design purposes	This value is affected by precipitation filter design and the use of drying air
Precipitate bulk density	1.3–1.5 t/m^3 at 50% moisture	

8. OPERATIONS

The Merrill–Crowe zinc-precipitation process has been applied worldwide on a large number of operations, both large and small. The main geographic areas where it has found widespread, large-scale application are as follows.

8.1. South Africa

The South African gold industry underwent a large expansion during the late 19th and most of the 20th century. Until the early 1980s most of these plants used the Merrill–Crowe process. One of the last Merrill–Crowe plants constructed was at Anglo American's Elandsrand mine. It used two-stage rotary-drum filtration, hopper clarification and zinc cementation with candle filters. The flowrate was typical of South African operations at around $400\,m^3/h$, although some were designed at up to $850\,m^3/h$. The backwashed precipitate was filtered and dried on a pre-coated rotary-drum filter and the filter cake was calcined overnight in a continuous-belt calciner. A number of the new CIP plants such as President Brand still use zinc precipitation for gold recovery from eluates as well as from solutions originating from intensive cyanidation.

8.2. Canada

A large number of the gold-processing plants that were built in the early to mid-20th century in the Kirkland Lake, Timmins, Val d'Or and Red Lake areas utilized zinc cementation. In British Columbia, zinc cementation is represented by the Nickel Plate mine, which was built in the mid-1980s using a design developed a few years earlier. This operation was characterized by high soluble-copper values.

8.3. USA

The major US operations were heap-leach plants and milling operations, which were built mostly in Nevada such as Coeur–Rochester and Paradise Peak. The original Lead operation owned by Homestake used the Merrill–Crowe process, as did some of the early Californian operations.

8.4. Mexico

The Merrill–Crowe zinc-cementation process is mainly applied to silver ores. However, some gold is also recovered using this route.

8.5. South America

South America has numerous applications using zinc-cementation, particularly in Peru. Larger recent applications operating in the 1,200 to $1{,}500\,m^3/h$ range are Minera Barrick's Pierina mine (1998) and Alto Chicama (2005), both in Peru. Yanacocha and Maqui–Maqui mines, also in Peru, represent Minera Newmont. In Chile, Placer Dome has the La Coipa mine, and Amax has the smaller Guanaco mine. One of the largest Merrill–Crowe plants built to date will be Barrick's Minera Argentina Gold's Veladero mine in Argentina, which is scheduled to be commissioned at 2,000 m^3/h in 2005.

8.6. Other

In Africa, Merrill–Crowe process is represented by Ashanti in Ghana and numerous smaller operations. The Zarafshan–Newmont project uses the Merrill–Crowe process at 1,065 m^3/h at their heap-leach project in Uzbekistan. Smaller Merrill–Crowe operations exist in India, Australia, Brazil and the Phillipines.

9. ADVANCES

The three main improvements to the Merrill–Crowe process that were initiated in the 20 years following the initial patenting and introduction of the process were the use of a lead salt, substitution of zinc powder in place of the zinc shavings, and the introduction of de-aeration through the use of a vacuum de-aeration tower. Since these developments, the main improvements to the process have been equipment related. Ongoing refinements have simplified operations, reduced operating costs and increased the size of plants.

As with other recent advances in mining and metallurgical technology, it is not only innovation that takes place but also application of an ever-increasing scale of operation. *Single-stream* zinc-cementation plants now operate in excess of 1,500 m^3/h; plants planned to operate at 2,000 m^3/h are now in construction and other larger ones, such as Barrick's Pascua Lama project, which straddles the Chile–Argentina border, are in the feasibility stage.

The use of the basic process has been expanded to include gold recovery from carbon-stripping eluates and solutions originating from the intensive cyanidation of gravity concentrates. The chemistry of these solutions can be similar. De-aeration is not required on hot eluates from carbon stripping, mainly due to their lower equilibrium oxygen content. Much higher cyanide solution strengths on the order of 2–5 g/L have been found necessary to precipitate the high gold concentrations in eluates of 20–100 mg/L, while preventing zinc hydroxide formation. Lead nitrate is generally not required. Zinc additions rates are closer to stoichiometric levels and the resultant precipitates are higher in gold (50–90%) and lower in zinc (3–10%) than typical zinc precipitates (Marsden and House, 1992). Eluates subjected to electrowinning are typically recirculated to reduce overall reagent consumption, but eluates which have been subjected to zinc cementation generally require a bleed to reduce soluble zinc concentrations. Some eluates from satellite processing operations are transported to a central conventional Merrill–Crowe plant and are simply *bled in* to the process. The volume ratios of these solutions are often such as to make any changes in overall chemistry almost undetectable.

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Ray Walton graduated in 1977 with a B.Tech, in Materials Science, from Brunel University, in Uxbridge, Middlesex, UK. He joined Anglo American Corporation of South Africa and worked in the Joint Metallurgical Scheme in the Orange Free State, which included the original President Brand, Merrill–Crowe plant. He then assisted in commissioning Elandsrand in the Western Transvaal, which was Anglo's last large Merrill–Crowe plant, and later worked at Ergo and Simmergo on tailings retreatment until 1986. These plants included Merrill–Crowe processing of solutions and eluates.

After managing a two-year program to develop a bacterial gold recovery process for a refractory gold tailings retreatment project in Northern Manitoba, he joined Kilborn Engineering of Toronto in 1987 and is now Principal Metallurgist with SNC Lavalin Engineers and Constructors in Toronto Canada, who took over Kilborn in 1996. He currently has 27 years of experience in process engineering, project management, commissioning and metallurgical plant operations, including consulting assignments, feasibility studies, project evaluations, engineering and commissioning on a variety of gold, copper, base metals, uranium and rare-earth metal recovery projects.

His recent projects have been the high volume Alto Chicama and Veladero gold heap-leach projects, which both use the Merrill–Crowe process, the Barrick Goldstrike dry grinding and roasting project, and the El Indio gold/copper/arsenic concentrate-roasting plant upgrade project. Ray has particular experience in certain aspects of the pyro- and hydrometallurgy of copper and gold.

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Chapter 25

Resin-in-pulp and resin-in-solution

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1. INTRODUCTION

After the development of cyanide processing of gold ores over a century ago, no significant advances in technology took place until the introduction of large-scale carbon-in-pulp (CIP) and carbon-in-leach (CIL) plants in the 1970s. CIP is today the preferred route in the western world for the recovery of gold from cyanided pulp. Information that emanated (Anonymous, 1987) from the former Soviet Union (FSU) indicated that a large proportion of gold produced in the FSU was produced via resin-in-pulp (RIP) or resin-in-leach (RIL), including the Muruntau operation that treated around 1.3 Mt of ore per month (McQuiston and Shoemaker, 1981).

Significant developments around gold-selective anion-exchange resins and the commercialization of at least two of these products have made RIP available in the western world as an alternative to CIP for the upgrading of gold from cyanided pulps. Gold-selective resins have some distinct advantages over activated carbon for the recovery of gold from cyanide-leach liquors. Resins have potentially higher loading capacities, higher loading rates, are less likely to be poisoned by organics and do not require thermal regeneration. The main disadvantage of gold-selective resins is that they are more

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expensive than activated carbon. However, despite their higher costs, they can be more cost-effective than activated carbon, primarily due to the fact that no regeneration of the adsorbent is required, resulting in capital and operating cost savings.

Developments in contacting equipment and advances in resin durability dispelled fears about problems with screening of resin from pulp, and of resins being physically too weak. A great improvement in elution methods (Fleming, 1985), commercial availability of gold-selective resins, and the successful implementation of some RIP and RIL plants in the western world, namely Golden Jubilee Mine (Fleming, 1989) and Barbrook Gold Mine in South Africa (Anonymous, 2003) and Penjom Gold Mine in Malaysia (Lewis, 2000), make RIP an attractive and viable alternative to CIP. Both the Golden Jubilee Mine and Penjom Gold Mine were conventional CIP/CIL plants that were retrofitted to RIP/RIL plants owing to the low gold recoveries obtained with carbon.

Although gold-selective resins have been commercially available for a number of years and three RIP plants have been successfully operated in the western world, RIP has had limited success despite the potential for capital and operating cost savings for new plants. It is believed that the primary reason for this is that CIP is an entrenched technology that has been in operation for more than three decades, and hence the risk of employing this technology is low. Furthermore, the capital and operating costs of the metallurgical plant are often low in relation to the mining costs. Nevertheless, more recently it has become clear that there are niche applications for RIP/RIL, mainly the recovery of gold from *preg-robbing* ores, where resin generally results in higher gold recoveries than carbon (see Chapter 38), and for the recovery of gold in areas where power is expensive. From testwork done at Mintek on many preg-robbing ores (Green *et al*., 2002), it is clear that for these applications RIP has a major advantage over CIP in that higher gold recoveries are attainable, which has a direct implication for the profitability of the operation. This has been demonstrated at the Penjom Gold Mine in Malaysia.

2. SOLUTION CHEMISTRY OF CYANIDED GOLD PULPS

The composition of the gold-leach liquor is critical for the selectivity of any adsorbent, and hence its performance. Gold as the aurocyanide anion ($Au(CN)_2^-$) is strongly adsorbed by anion-exchange resins from alkaline cyanide solutions. Base-metal cyanides (*e.g.*, $Cu(CN)_3^{2-}$, $Zn(CN)_4^{2-}$, $Ni(CN)_4^{2-}$, $Co(CN)_5^{3-}$, $Fe(CN)_6^{4-}$), which also load favourably, are generally present in leached gold pulps and they will therefore compete for the limited number of sites on the resin. Thus, the capacity of an anion-exchange resin for gold depends strongly on the relative affinities of the functional group for the different anions in the pulp, the spacing of the functional groups, and the relative concentrations of these anions in solution. Work done by various groups over the years has shown that the subject of selectivity is very complex and depends on properties of the anions in question, the structure of the resin and the relative loading rates of the anions.

The pioneering work in the area of chemistry of the anions in relation to ion exchange was carried out by Aveston *et al.*, (1958), and since then very little further progress has been made in elucidating the properties of the different metal-cyanide complexes that affect their affinities for resins. Adsorption of anions on both strong- and weak-base ion-exchange resins seems to be a function of the charge, polarizability and, to a lesser extent, shape of the anion. For anions with the same charge and shape (*e.g.*, halides) it was shown that the log K_d value (K_d is the molal selectivity coefficient) is linearly related to polarizability, with the larger and more polarizable anion, I^-, being bound more strongly. The slope of the plot of log K_d vs. ionic refraction (a measure of polarizability) confirmed the prime importance of polarization forces in anion exchange as opposed to coulombic forces in cation exchange processes. Owing to the greater interaction between resin sites and adsorbed anions, caused by the polarization forces, bonding is due to ion-pair formation (as opposed to electrostatic interaction in the case of cation exchange).

Aveston *et al.* (1958) gave the order of selectivity of a strong-base resin for metal cyanides as Au > Ni > Co, Fe. The high affinity of the resin for gold cyanide was ascribed to concentration of polarization forces along the axis of the linear molecule. They found that although bivalent ions such as nickel(II) *tetra*cyanide and the trivalent ions such as cobalt(III) *penta*cyanide are also highly polarizable, they are less strongly adsorbed. The greater average distance between positive resin sites and the multivalent anion compared with that of a single resin site and a univalent anion such as gold cyanide was given as the reason for this.

3. DEVELOPMENT OF GOLD-SELECTIVE RESINS

Except for changes in the properties of the less-stable metal-cyanide ions, which can be affected by altering the cyanide concentration or pH value, there is nothing that can be done to the solution to influence the preference of a resin for gold over the base-metal cyanides. The alternative, therefore, was to alter the structure of the resin. Aveston *et al.* (1958) suggested that an increase in the average distance between positive resin sites should decrease the affinity of the resin for multi-charged anions. This was confirmed by Clifford and Weber (1983). This property could be achieved by:

(i) Lowering the functional group content of the resin. This was the basis on which the Minix resin was developed.
(ii) By using a mixture of secondary and tertiary amines during functionalization of the resin. This also results in an increase in the distance between the active sites, as the secondary amine would be in the free-base form at the high pH of loading from a cyanide-leach liquor. The AM2B resin that is being used industrially in the Commonwealth of Independent States is based on this strategy.

There are two types of gold-selective resins commercially available on the market, namely medium- and strong-base anion-exchange resins. A medium-base resin generally has the primary advantage that it could be eluted or stripped with aqueous NaOH, while the most important advantage of a strong-base resin is that its performance is independent of the pH value of the leach liquor.

3.1. Strong-base resins

Strong-base anion exchangers possess active sites with fixed positive charges and the sites are generally quaternary ammonium groups resulting from the reaction of a tertiary amine with a chloromethylated polystyrene matrix, as shown in the following equation:

$$\mathrm{P-CH_2Cl+NR_3 \rightarrow P-NR_3^+Cl^-} \tag{1}$$

where P represents the polymer matrix and R an alkyl chain.

A gold or other metal-cyanide anion can displace the counter-ion associated with the positively charged site on the resin and become attached by the formation of an ion pair. Metal-cyanide anions are highly polarizable, so they bond strongly to the resin. The reaction is independent of solution pH value, and therefore loading at the high pH value of a cyanide-leach liquor, and variations in the adsorption pH value do not have an effect on the performance of the resin, as illustrated in the following equation:

$$\mathrm{P-NR_3^+Cl^-+Au(CN)_2^- \rightarrow P-NR_3^+Au(CN)_2^-+Cl^-} \tag{2}$$

The Minix resin is an example of a strong-base resin, and contains *tri*butylamine as functional group (Kotze *et al.*, 1993). Conventional strong-base resins, which are generally employed in the water-purification industry and for the recovery of uranium, contain *tri*methylamine as the functional group.

3.2. Medium-base resins

For conventional medium-base anion exchangers, the active groups are generally derived from primary or secondary amines. The functional groups on the resin are thus either secondary or tertiary amines, which have no permanent charge and must be protonated (Eq. (3)) before the resin can interact with a metal-cyanide anion (Eq. (4))

$$\text{Protonation}: \ \text{P} - \text{NR}_2 + \text{H}^+ \rightarrow \text{P} - \text{NR}_2\text{H}^+ \tag{3}$$

$$\text{Adsorption}: \ -\text{NR}_2\text{H}^+\text{CI}^- + \text{Au(CN)}_2^- \rightarrow \text{P} - \text{NR}_2\text{H}^+\text{Au(CN)}_2^- + \text{CI}^- \tag{4}$$

Therefore, the greater the number of protonated amine groups on the resin at a specific pH value, the greater is the potential for a high gold-loading capacity. The extent of amine protonation at a specific pH value is determined by the basicity, or pK_a value, of the functional group on the resin. The effect of basicity of the functional group on loading and elution of a medium-base resin is illustrated in Fig. 1.

Elution of a medium-base resin is accomplished simply by reversal of the above reaction. An alkali, which will cause deprotonation of the resin, removes the positive charge and the metal-cyanide anion, which has no affinity for a neutral resin, will be stripped off the resin. The commercially available AuRIX® resin is a medium-base resin that contains guanidine as the functional group (Mackenzie, 1993). Guanidine has a relatively high pK_a value (~13.5), so that the resin has a reasonably high capacity at the pH value of cyanide-leach liquors.

3.3. Weak-base resins

Although the ultimate drive in resin development has been the development of a weak-base resin for gold recovery, the basicities of conventional

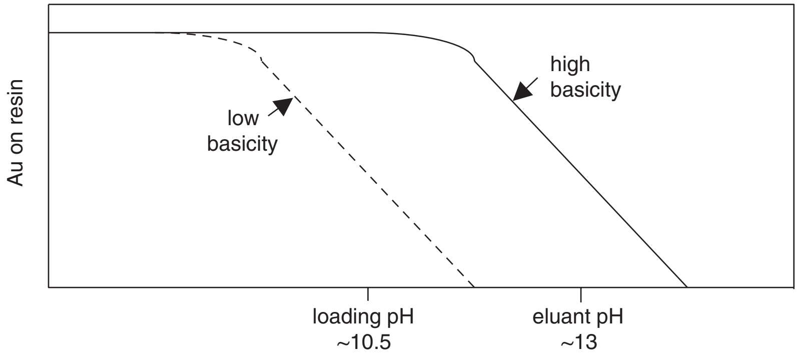

Fig. 1. Effect of functional group basicity on degree of protonation and gold loading.

weak-base resins are too low to render them useful for the recovery of gold cyanide from cyanide-leach liquors at pH values above 10.

3.4. Other resin types

Some resin types react according to another loading mechanism that is not based on ion exchange. Certain neutral polymeric adsorbents have been found to load gold from cyanide solutions (Adams *et al.*, 1987; Akser *et al.*, 1986, 1987). A mechanism was proposed that involves the adsorption of an ion-pair species $M^+Au(CN)_2^-$ on the surface of the polymer. Loading is promoted at increased ionic strength. Stripping is facilitated by the employment of a low ionic-strength eluant at high temperature. Resins found to be effective are high surface-area Amberlite (XAD) adsorbents and polystyrene matrices functionalized with phosphate-ester groups.

This discussion of resin structures that might be used to recover gold cyanide does not take into account special resins for gold that are of no particular industrial significance at this stage.

4. ELUTION OF DIFFERENT RESIN TYPES

The elution or stripping properties of a resin is as important as its loading performance. The functional groups on resins have different properties, including the strength of the ionic bond; elution methods therefore have to be developed and optimized for each resin type.

4.1. Elution of minix strong-base resin

Recognized methods of elution of strong-base resins use zinc cyanide, ammonium thiocyanate or acidic thiourea. Although each method has advantages and disadvantages (Fleming and Cromberge, 1984), no single method seems to be appropriate for all cases. For example, Fleming (1989) employed the zinc-cyanide method for a conventional strong-base resin (A161RIP) used at the Golden Jubilee RIP plant, while for a more selective resin such as Minix, the thiourea method is more effective. Advantages of this stripping procedure are that no regeneration of the resin is necessary and elution is faster, as illustrated in Fig. 2.

The most effective elution technique for Minix makes use of acidic thiourea after an acid wash (1 M) to remove nickel, zinc and some copper. The gold-selective adsorption characteristics of Minix, particularly its high selectivity against cobalt and iron, make it possible to use its advantages (fast kinetics and circuit simplicity) without fear of poisoning the resin (Fleming and Hancock, 1979), as is the case with other commercially available strong-base resins. Elution can be improved by an increase in the thiourea concentration, the acid concentration or the temperature. With an eluant containing 1 M

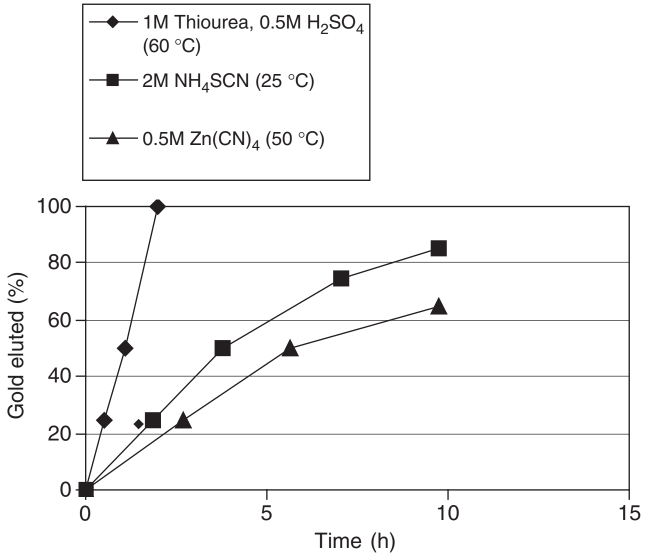

Fig. 2. Elution of Minix gold-selective resin with various eluants.

thiourea and 0.5 M H_2SO_4 at 60°C, elution efficiencies of more than 99.6% can be effected within 4–5 bed volumes of eluant. Using this elution strategy, the resin is easily stripped to below 100 g/t of residual gold.

Electrowinning has proven to be an effective and simple method for recovering gold from the eluate. Electrowinning is done simultaneously with the elution. The barren eluate is recycled to the eluant tank and is recycled for the next elution after the reagents have been made up to their relevant concentrations. Two operating plants, namely Penjom Gold Mine and Barbrook Gold Mine, have now demonstrated the feasibility of this elution strategy for Minix with simultaneous electrowinning.

4.2. Elution of AM-2B resin

Elution of AM-2B resin is similar to that of Minix; however, a longer elution time seems to be required (Bolinsky and Shirley, 1996). The process includes a series of elutions, contacting the loaded resin with different solutions. The elution flowsheet differs from plant to plant, and some of the steps described below are optional. Usually the following steps are carried out:

- stripping of Fe and Cu with sodium cyanide (40 g/L containing 1.5 g/L NaOH);
- stripping of Zn and Ni with dilute sulfuric acid (50 g/L);
- optional stripping of silver with thiourea solution, used only when large quantities of silver are present in the solution;

- two-stage stripping of gold with thiourea solution (80 g/L containing 25 g/L H_2SO_4), and
- regeneration of the resin, converting it back to the OH^- form for the quaternary groups and the tertiary groups are deprotonated by contacting the resin with sodium hydroxide solution.

All of the stripping operations are carried out at 55–60°C and atmospheric pressure. The original design of the stripping section required up to 288 h (12 days) for elution before achieving gold recovery. In the 1980s, a new stripping technique was developed, which takes from 12–24 h, a considerable improvement over the original design. Gold from the pregnant thiourea solution is recovered by transferring the solution from the elution section to holding tanks for an electrowinning section. During electrowinning, the solution is circulated between the holding tanks and electrowinning cells. Residual gold on the stripped resin is expected to be below 100 g/t.

4.3. Elution of AuRIX® resin

Combining the elution and electrowinning operations enables elution of AuRIX® 100 to be achieved by continuous electroelution using an eluate solution based on 1 M sodium hydroxide at 60°C (Mackenzie, 1993). In this process, the eluate is passed through a bed of resin and is continually recycled through an electrowinning cell back to the resin bed. In some instances, an improvement to the elution rate can be obtained when the alkaline eluant contains a low concentration of alkali metal cyanide salt and an alkaline salt of a carboxylic acid such as sodium benzoate (Virnig, 1996).

The elution of AuRIX® 100 resin was studied exhaustively in a pilot plant in Mexico (Fisher *et al.*, 2000). Initially, resin elution was performed with an eluate composition of 40 g/L NaOH, 70 g/L sodium benzoate, and 100 mg/L free CN. Total eluate volume in the circuit was 64 L. Sodium benzoate was found, in bench-scale testing, to accelerate elution kinetics. Elution was carried out at 60°C for 6 h. At termination of elution, the difference between the gold concentration in the eluant entering and the eluate exiting the column was less than 1 mg/L Au. Elution profiles (eluate exiting the column) typical of the sodium benzoate-containing eluate are shown in Fig. 3. Loaded and eluted resin analysis for a sample using this eluate is given in Table 1.

Elutions were also carried out without sodium benzoate. Fig. 4 shows the effect of sodium benzoate in altering the elution profile. At the end of 6 h, the same differential between the eluant entering and eluate exiting the column (less than 1 mg/L Au) was obtained. Therefore, sodium benzoate was not a necessary addition for elution of AuRIX® 100. Eluate produced by this type of resin is suitable for conventional gold electrowinning with single-pass

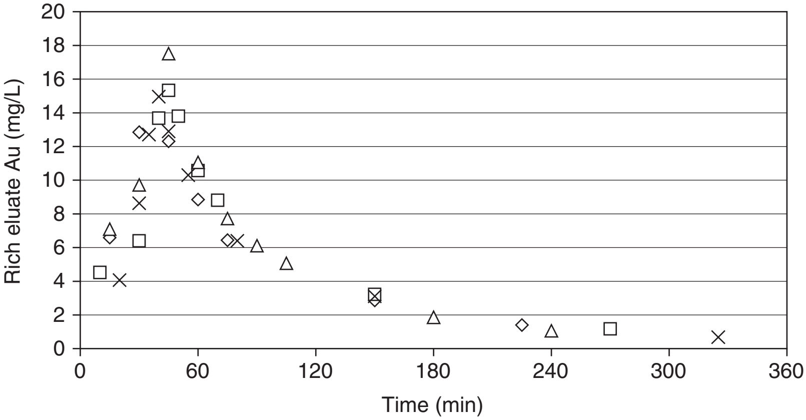

Fig. 3. Rich-eluate profiles vs. time for AuRIX® 100 resin.

Table 1
Loaded and eluted resin analysis for AuRIX® 100 Resin

Sample	Au (mg/kg)	Ag (mg/kg)
Loaded	1,720	393
Eluted	163	83

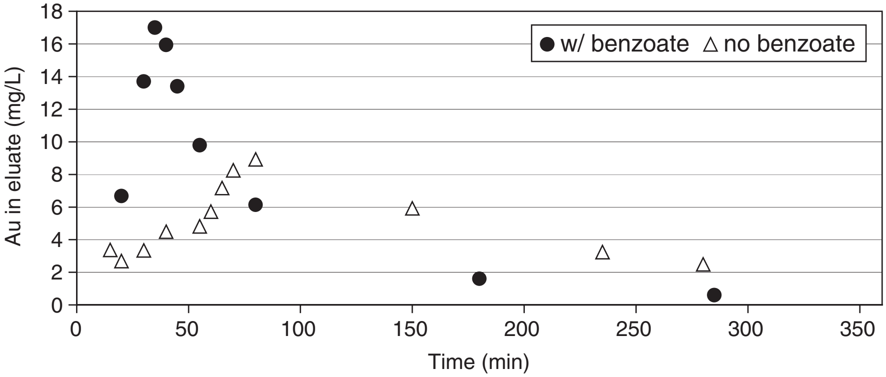

Fig. 4. Rich-eluate profile comparison.

efficiencies of 66.5–91.7% and overall gold recovery in electrowinning of 94.5–99.8%.

4.4. Elution of conventional strong-base resins (A161 L, A161RIP, Vitrokele 912)

A conventional strong-base resin (Duolite A161L) was used at the Golden Jubilee Mine for the recovery of gold, primarily due to the fact that no gold-selective resin was commercially available in the western world at that stage. The zinc-cyanide elution process is suitable for all non-selective strong-base resins. It is a reversible reaction and therefore, in order for the reaction to proceed to completion, it is important that the concentration of gold in the eluate should be kept as low as possible. This can be done either by the use of a very large volume of eluant, which is pumped in a single-pass through the elution column (this is clearly an impractical and expensive approach), or by the use of the electroelution method, in which eluate solution is recirculated continuously between an electrowinning cell and the elution column. The latter approach was adopted at Golden Jubilee (Fleming and Seymore, 1989) and made use of the Mintek-designed electrowinning cell.

In the Golden Jubilee elution, one bed-volume of solution containing approximately 0.6 M $Zn(CN)_4^{2-}$ was re-circulated from a surge tank through a heating box, elution column, and an electrowinning cell, back to the surge tank. After about 6 h of elution at 60°C, zinc oxide and sodium cyanide were added to the eluate to compensate for the zinc cyanide that had loaded onto the resin and to restore the concentration in solution to the starting value of 0.6 M.

The major disadvantage of the zinc-cyanide electroelution process is that it is slow; for the first 6 months each elution cycle was continued for a period of 4–5 days. However, since only one elution was necessary per week, the slow elution did not create a bottleneck in the process. Moreover, it was possible to systematically reduce the elution time over 12 months of operation, mainly as a result of improvements to the efficiency of the electrowinning process, to attain an ultimate elution period of 48 h.

After elution, the resin was washed with water to remove entrained zinc cyanide solution and the resin was then regenerated with 1 M sulfuric acid solution. The spent regenerant solution, containing zinc sulfate saturated with hydrogen cyanide gas, was pumped directly into a stirred lime slurry. The zinc cyanide that was produced during this neutralization reaction could be recycled to elution.

Vitrokele is a generic name given to the specialist technology that has been developed for the recovery of cyanide from precious-metal plant process streams (Signet Engineering, 1996) and the recycling of cyanide within the circuit. The resin that has been developed for gold-processing applications, Vitrokele 912, is manufactured by Rohm & Haas in France. It is understood that the technology was commercially applied at the Connemara plant in Zimbabwe for gold recovery by means of resin-in-solution (RIS) and that significant capital cost savings were realized by use of the resin in place of the conventional activated-carbon process. The flowsheet given for the process suggests that similar chemistry to that used at the Golden Jubilee plant (Fleming, 1989) was employed. Therefore, it is thought that the resin used was probably a strong-base anion exchanger similar to the A161L resin.

5. RESIN EVALUATION TECHNIQUES

The various gold-selective resins, conventional resins and activated carbon all contain different active groups, so they behave differently in cyanide-leach solutions. It is therefore critical that the performance of an adsorbent be evaluated for a specific application. There are a number of simple techniques that can be used to compare adsorbents on an equal basis.

5.1. Mini-column loading tests

These tests (Kotze *et al.*, 1993) involve the loading of a small volume of resin (1 mL) into a mini-column (1 cm diameter; 5–10 cm high) and passing a ‘standard’ synthetic cyanide-leach liquor through the resin bed over an extended period of time to ensure that the adsorbent is close to equilibrium with the feed solution. It is recommended that a ‘standard’ synthetic solution be used if these tests are done for the development of adsorbents, as it allows the tests to be repeated under very controlled conditions. Conditions that could be used for this type of test are as follows:

- Solution composition (mg/L, referred to as ‘standard’ solution): Au (5), Ag (0.5), Zn (2), Ni (5), Co (1), Fe II (5), Fe III (5), Cu (10) as cyanide complexes, at a pH of 10.5.
- Solution flowrate: 2.5 mL/min.
- Period of flow: 72 h.

At completion of the loading test, the loaded resins are rinsed with water (four bed volumes), dried and analysed for the various metals present in the feed. Results obtained with some adsorbents using this technique are given in Table 2.

Table 2
Results obtained with column loading tests on some adsorbents

Adsorbent	Metal on resin (mg/kg)							Au[a]/M
	Au	Ag	Zn	Ni	Cu	Co	Fe	
Activated carbon	25,200	<200	<200	460	<200	<200	1,500	0.93
A161L	13,300	<250	9,000	18,000	15,800	4,600	21,300	0.16
Minix	36,300	300	10,000	7,300	1,200	<330	<330	0.65

[a] The ratio of gold loaded onto the resin (mg/kg) to the total metal loading on the resin (mg/kg) is a measure of the selectivity of the resin for gold over the other base-metal cyanides.

The results indicated that the Minix resin exhibited the highest gold-loading capacity from this particular synthetic solution where there were significant concentrations of base metals present. Although the gold-loading capacity of activated carbon was lower than that of Minix, it remains the most selective adsorbent for gold. The commercial strong-base resin, A161L, had a relatively low gold-loading capacity owing to its poor selectivity for gold over the base-metal cyanides.

5.2. Counter-current ion-exchange tests

Counter-current ion-exchange (CCIX) tests (Kotze *et al.*, 1993) generally give a very good indication of how an adsorbent will behave in a carousel mode of operation. A number of mini-columns are set up in series and the pregnant solution is passed through the columns, counter-currently to the movement of the columns. At transfer, the loaded resin column (column where feed enters) is removed at pre-determined intervals, the second column becomes the first column, and a column containing stripped or fresh resin is added to the column train at the back. The solution is fed into the first column and the barren solution exits the last column. This process has to be continued until steady state is achieved, i.e., the solution profile across the system remains constant at transfer. If the gold concentration in the barren is too high, or the gold concentration in the solution exiting the last few columns is close to the desired barren, the solution flow rate has to be either decreased or increased, respectively. This is continued until the desired barren tenor is achieved. Solution and adsorbent profiles are then determined at steady state.

Solution and resin profiles for the CCIX tests in a ‘standard’ synthetic solution (composition given above) are given in Table 3 for a comparison between Minix, A161 and activated carbon. A comparison of the optimum gold loadings of the different adsorbents showed that the Minix resin is superior to the other adsorbents for a medium gold-grade solution. Minix achieved a gold loading of almost 60% more than that obtained with carbon. The strong-base resin A161 RIP loaded poorly. The composition of the solution, particularly with respect to copper and iron, adversely affected the gold loading of this non-selective resin.

5.3. Equilibrium isotherm

Equilibrium isotherms are critical for understanding the performance that could be expected of any adsorbent in operation. The adsorption of gold by an adsorbent is usually a reversible reaction, and therefore an equilibrium exists between gold in the solution and gold on the adsorbent. The degree of gold loading attainable with an adsorbent in operation depends on three

Table 3
Gold profiles from CCIX tests: ‘Standard’ liquor at steady state (optimum recovery conditions)

Adsorbent	Volume, (ml) (mass, g)	Solution flowrate (BV/h)	Gold concentrations leaving stage (mg/L)							
			Stage							
			Head	1	2	3	4	5	6	7
Minix I	8 (2.48)	75.75	4.7	3.3	1.91	0.97	0.41	0.160	0.039	0.008
A161 RIP	8 (2.34)	33	4.7	3.7	2.20	0.80	0.29	0.063	0.013	<0.001
Carbon	6 (2.88)	70	4.8	3.6	1.90	0.77	0.24	0.047	0.010	<0.002
				Calculated gold concentrations on adsorbent (mg/kg)						
				Stage						
				1	2	3	4	5	6	7
Minix I		75.75		27,200	19,100	11,200	5,700	2,400	890	180
A161 RIP		33		12,700	10,000	6,000	2,200	780	170	30
Carbon		70		16,800	12,420	6,600	2,700	830	160	30

factors, namely:

- the theoretical ion-exchange capacity of the adsorbent;
- the selectivity of the adsorbent for gold cyanide over the other anions present in the leach liquor; and
- the rate of approach to equilibrium loading.

The operating parameters of a plant are set to achieve the highest practical loading on the adsorbent, for an acceptable gold concentration in the barren (usually less than 0.01 mg/L). Higher adsorbent loadings mean lower adsorbent flowrates, which would result in lower capital and operating costs. It is impractical to achieve complete equilibrium loading capacities with any adsorbent under conditions experienced in a plant. Complete equilibrium loading on a resin can be achieved within a reasonable time period (days), but carbon would take weeks to reach its equilibrium capacity (Fleming, 1988). Thus, kinetics of adsorption is a further important parameter in the comparison of resins and carbon.

Equilibrium isotherms are constructed by contacting a measurable volume of resin with various volumes of the specific leach liquor or pulp under investigation. The equilibrium reaction is then allowed to take place over the time period that the adsorbent is expected to spend in the adsorption circuit. The solution phases of the leached pulp and those after completion of the batch tests are analysed for gold and the gold loading of the adsorbent can be calculated.

The data obtained with the equilibrium tests are analysed by fitting a Freundlich isotherm to the data. The Freundlich isotherm states that

$$C_e = a(S_e)^b \tag{5}$$

where C_e is the equilibrium concentration of gold on the adsorbent; S_e is the concentration of gold in solution at equilibrium; and a,b are the Freundlich constants.

This is the isotherm that is generally used, but any of the other equations describing equilibrium isotherms, such as the Langmuir isotherm could also be used.

5.4. Kinetics

The rate of extraction of gold cyanide by resins and activated carbon is controlled by film diffusion in the initial stages (less than 30% of gold loading) and by both film and intra-particle diffusion in the latter stages, as equilibrium is approached (Fleming and Nicol, 1984). During the initial stages, therefore, the rate of loading will be similar for resins and carbon and will only differ as a result of the difference in size of the resin beads (typically 0.85–1.0 mm in diameter) and the carbon granules (typically, 1.0–3.0 mm). Under film-diffusion-controlled conditions, the rate of loading is inversely proportional to the mean particle-diameter of the extractant, and therefore, the rate of extraction by resins will be about twice the rate of extraction by carbon.

However, the disparity between the loading rates of resin and carbon increases as equilibrium is approached and particle diffusion becomes significant. Under these conditions, the rate of extraction by resins is at least an order of magnitude faster than the rate of extraction by carbon. The reason for this is the fact that most of the surface area of carbon is available for adsorption only after extremely slow diffusion of the gold cyanide through micropores whose cross-sectional areas are similar to those of the gold-cyanide anion. On the other hand, the pores of ion-exchange resins (particularly the macroporous type), which are large and have a fairly uniform pore-size distribution, allow gold cyanide to diffuse rapidly to the centre of the resin beads (Fleming, 1988). Furthermore, the rate of particle diffusion is inversely proportional to the square of the mean diameter of the particle, and as a result of the smaller particle sizes of ion-exchange resins when compared with activated carbon, their particle-diffusion rates will be much higher than that of activated carbon.

The kinetic test is also done in batch mode and specified amounts of pulp and adsorbent are contacted in a mechanically agitated tank specifically designed for this purpose. The conditions under which this test is done are carefully controlled. At specified time intervals, samples of the pulp are withdrawn and immediately filtered. The filtrates are analysed for gold.

The data obtained from the kinetic tests are analysed by fitting a rate expression to the data (Johns, 1996). The rate expression used is based on the classical expression for film-diffusion rate with the equilibrium being described by the Freundlich isotherm

$$r = k(A_c/V_s)\rho_s(S - b\sqrt{C/a}) \tag{6}$$

where r is the rate of gold adsorbed; k is the mass-transfer coefficient; A_c is the external surface area of adsorbent; V_s is the volume of solution; ρ_s is the density of solution; S is the concentration of gold in solution; and C is the gold loaded onto adsorbent.

As the rate-controlling step changes from film diffusion to intra-particle diffusion as the adsorbent becomes loaded towards its equilibrium value, the mass-transfer, coefficient is set as a function of the degree of loading on the adsorbent towards its equilibrium value

$$k = k_o[1 - (C/C_e)]^i \tag{7}$$

where k_o is the initial mass-transfer coefficient, and i is the fall-away in kinetics parameter.

5.5. Simulation of an adsorption circuit

The Freundlich *a* value and the mass-transfer coefficient are difficult to interpret in isolation. A method for the linking of the thermodynamic number (Freundlich *a*) and the kinetic number (*k*) involves their use to simulate or model an adsorption circuit (Johns, 1996). The adsorption-rate expression is used in conjunction with a continuous stirred-tank reactor (CSTR) mass balance to mathematically describe the operation of an adsorbent-in-pulp circuit. A seven-stage model, developed by Mintek, dynamically describes the solution concentration and adsorbent loading with time, and takes into account the active volume of the tank and pulp bypass. Thus, the thermodynamic and kinetic dimensions are combined and converted into a gold-loading value on the adsorbent in a counter-current plant. This determines the overall adsorbent inventory, the inventory per stage and the flow of adsorbent. The elution plant can be sized accordingly.

The model and the results of the in-pulp tests were used in a determination of the loading on the adsorbent at which a barren concentration of less than 0.01 mg/L is obtained from a feed of 5 mg/L. A plant was assumed to treat 100 kt of pulp per month in a seven-stage adsorption plant. The residence time of the pulp was set at 0.5 h per stage for carbon and 0.25 h per stage for resin. The residence time of the adsorbent was set at one day per stage. The diameter of the carbon particle was set at 1.4 mm, and that of the resin particle at 0.95 mm. Results obtained with the simulation are given in Table 4.

To quantify the effect of the Freundlich *a* value and the mass-transfer coefficient on the performance of a typical adsorption plant, the simulation described above was used. To illustrate the effect of the equilibrium isotherm, the Freundlich *a* value (a measure of the loading) was varied and the effect on the solution profile obtained is shown in Fig. 5.

The more favourable the equilibrium isotherm (i.e., an increase in the *a* value), the lower the solution barren exiting the adsorption plant. An increase in the *a* value from 5,000 to 10,000 to 20,000 resulted in the lowering of the barren from 0.023 to 0.007 to 0.004 mg/L.

To illustrate the effect of kinetics, the *k* value, which is a measure of the mass transfer, was varied. The effect on the solution profile is shown in

Table 4
Results of simulation for Minix and carbon

Adsorbent	Adsorbent concentration (g/L)	Upgrading ratio[a]	Gold loading[b] (g/t)
Carbon, ANK 11	24	1,460	7,500
Minix	18	3,890	19,920

[a] Upgrading ratio is the ratio of solution flowrate (mass) to resin flowrate (mass).

[b] Gold loading as predicted by the simulation.

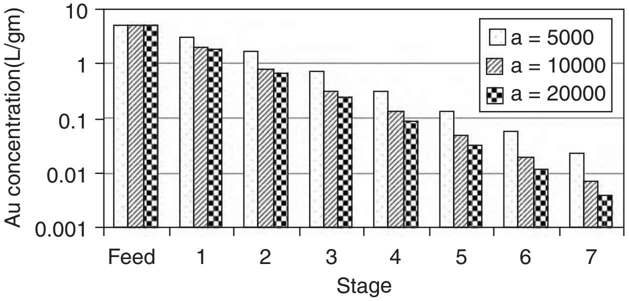

Fig. 5. Effect of equilibrium isotherm on plant performance.

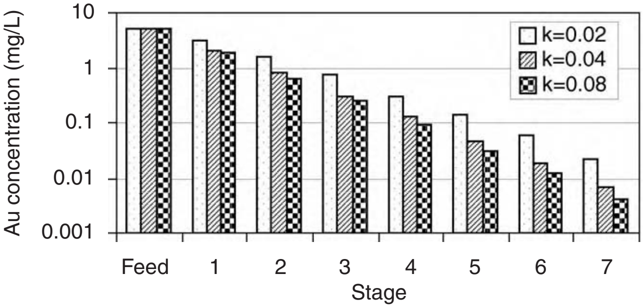

Fig. 6. Effect of mass-transfer coefficient on plant performance.

Fig. 6. The more favourable the kinetics, the lower the solution barren exiting the adsorption plant. An increase in the *k* value from 0.02 to 0.04 to 0.08 m/h results in the lowering of the barren from 0.055 to 0.007 to 0.001 mg/L.

These simulated results indicated that the effect of changing the mass-transfer coefficient is more pronounced than the effect of changing the equilibrium isotherm.

5.6. Resin strength and durability

An important factor to consider when selecting a resin for use in an in-pulp system is the resistance of the resin beads to degradation during processing. Resin breakage can occur as a result of

- *abrasion* of the resin particle by the fine particles of the pulp;
- *shattering* of the resin bead due to impact caused by mechanical handling of the resin, i.e., pumping, screening and mixing; and
- *osmotic shock*, where the resin swells and shrinks significantly during successive adsorption/elution cycles.

Durability is a critical property, because

- resins are generally more expensive than activated carbon. Therefore, resin losses would have to be limited so that the operating costs associated with adsorbent replacement are similar to or lower than those for activated carbon; and
- resins are expected to have higher gold-loading capacities and kinetics than activated carbon. In order to limit gold losses associated with the loss of resin, it is crucial that the resin be made durable.

Therefore, durability is an important component of resin evaluation. If the metallurgical performance of a resin is good, it should be subjected to a durability test to give an idea of losses on a full-scale plant.

Experience at Mintek suggested that in order to establish the durability of an ion-exchange resin in a pulp, the resin must be subjected to

- a *chemical* treatment (similar conditions to those that it will be exposed to during successive adsorption/elution cycles); and
- a *physical* treatment, in which the resin is contacted with pulp, in a manner that will produce measurable degradation.

Thus, the test method adopted accelerates the rate of attrition by subjecting a batch of resin to repeated cycles of aggressive agitation in pulp, preceded by H_2SO_4 and NaOH washing. A summary of the operating conditions is shown in Table 5.

Table 5
Summary of operating conditions for accelerated degradation test (Initial resin volume, 200 mL; free-wet settled; 100% > 600 μm)

Reagent	Concentration (g/L)	Duration (min)
Chemical treatment step		
H_2SO_4	200	30
H_2O		60
NaOH	80	30
H_2O		60
Pulp attrition step		
Contacting vessel	Flat-bottomed tank	
Mechanical agitator	Axial	
Agitator speed	750 rpm	
Pulp density	1,400 kg/m^3 (46% solids)	
Pulp volume	2.0 L	
Duration	24 h	

The resin is subjected to six cycles of chemical and physical treatments. Losses in volume as well as the change in the bead size diameter are determined after every cycle. Resin losses experienced during the first cycle of this test might be misleading, as a higher breakage due to the presence of some weak beads could occur. It is necessary to do a full evaluation involving a minimum of six complete cycles on the most promising resin, to allow for a more accurate prediction of *life span*. Mintek evaluated resin durability on a 100 kt/mo (ore throughput) contactor at the Kloof Gold Mine in South Africa, using the Duolite A161L resin. This evaluation incorporated all the resin/pulp mixing, transportation and separation that would be encountered on an air-agitated plant (MINRIP^{TM}), using airlifts for resin transport. The resin was also submitted to acid and alkali treatments for each cycle. From this evaluation, the resin loss of this resin was determined to be 8 g/t. A comparison of these results with the results obtained in the laboratory test, for the same resin and other resins, gives an idea of the life span that can be expected of resins in an operating plant.

After each attrition cycle a screen analysis of the resin is performed and the d_{50} value is calculated (d_{50} is the aperture that 50% of the resin volume will pass through). The total resin inventory is screened at 600 μm and the volume of the oversize fraction of the 600 μm screen is measured and passed on for further treatment. A typical set of results for three resins is given in Table 6.

Table 6
Results of durability tests

Resin type	Size fraction (μm)	Volume (mL)		d_{50} (μm)		Conclusion
		Initial	Final	Initial	Final	
Resin A	1,180	10.5	6.37	843	834	Good (volume loss = 0%)
	850	78	79.5			
	600	13.5	16			
		102	102			
Resin B	1,180	10.5	3.2	846	829	Acceptable (volume loss = 1.8%)
	850	80.5	81			
	600	10	15			
		101	99.2			
Resin C	1,180	9.5	0.2	825	799	Unacceptable (volume loss = 11.1%)
	850	60	52.5			
	600	32	37.5			
		101.5	90.2			

6. RELATIVE COST COMPARISON OF RIP VS. CIP

The equilibrium and kinetic response of Minix and carbon were used as part of a preliminary techno-economic comparison between CIP and RIP employing MINRIP$^{\mathrm{TM}}$ (Johns and Marsh, 1993). The MINRIP$^{\mathrm{TM}}$ technology involves air agitation and airlifts for the transportation of resin. The costing of the adsorption facilities encompassed the tank farm, adsorbent inventory, interstage screens and pumps, compressor and samplers. The adsorbent inventory was assumed to be nine stage-inventories. The CIP tanks (flat-bottomed, mechanically agitated) were sized for 30 min pulp residence time per stage, while the RIP tanks (conical-bottomed, air agitated) were sized for 15 min pulp residence time per stage. Seven adsorption stages were assumed for both plants. The CIP interstage screens were NKM screens and carbon transfer was carried out by vertical-spindle recessed-impeller pumps. The RIP interstage screens were external sieve-bends onto which the pulp and resin were lifted by means of airlifts.

The costing of the elution facilities encompassed all elution, thermal regeneration and acid-washing equipment, and the reagent dosing and storage facilities. It was assumed that carbon would be stripped at 130°C in a 316 stainless-steel column, gold would be recovered by electrowinning, regeneration would be done in rotary kilns, and acid washing of the carbon after regeneration would be done in mild-steel, rubber-lined columns. For Minix, an acid wash (to strip most of the base metals) and the elution of gold and silver with acidic thiourea would be done in the same column (mild steel, rubber-lined, 60°C). Gold would be recovered by means of direct electrowinning from the eluate. One elution per day was assumed. Leach and smelt-house facilities were excluded from the costs, but purchasing, erection and installation were included. The costs were normalized by assuming that the cost of the adsorption section of a 25 kt/mo CIP plant would be equivalent to 1,000 (Johns & Marsh, 1993).

In the case of a plant treating 25 kt/mo of ore and producing 'standard' leach liquor (composition specified in Section 5), the relative costs for CIP and MINRIP$^{\mathrm{TM}}$ plants for the different cost elements are given in Figs. 7(a) and (b). The potential cost savings in capital (CAPEX) and operating expenditure (OPEX) for a MINRIP$^{\mathrm{TM}}$ plant relative to a CIP plant for three types of solution and for different production rates are given in Table 7. The cost study indicated that the MINRIP$^{\mathrm{TM}}$ process compared favourably with CIP for all three solution types.

The following observations were made from the cost estimates done for the various plant sizes:

- The capital cost of the adsorption section of the MINRIP$^{\mathrm{TM}}$ process is similar to that of CIP in most cases. The lower the tonnage, the more advantageous the MINRIP$^{\mathrm{TM}}$ operation becomes.

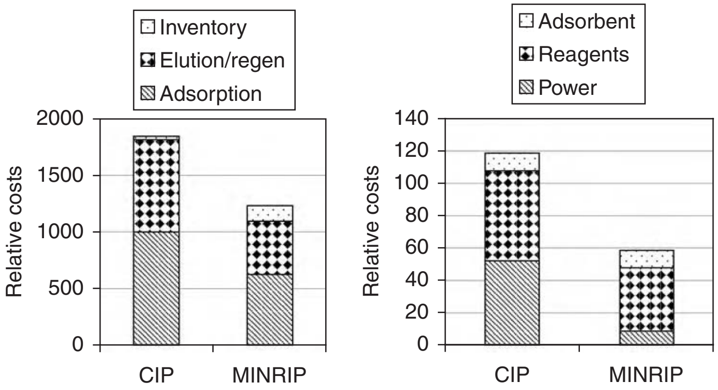

Fig. 7. Relative (a) CAPEX and (b) OPEX for CIP and MINRIP plants.

Table 7
Predicted cost savings for MINRIP^{TM} over CIP

Costs	Cost Saving for MINRIP^{TM} over CIP (%)			
	10 kt/mo	25 kt/mo	150 kt/mo	300 kt/mo
Dump solution				
Composition (mg/L): Au (0.5), Ag (0.05) Zn (1), Ni (10), Co (1), Cu (10), Fe (2)				
CAPEX	17	31	15	10
OPEX	46	44	33	28
Standard solution				
Composition (mg/L): Au (5), Ag (0.5) Zn (2), Ni (5), Co (1), Cu (10), Fe (10)				
CAPEX	20	33	22	13
OPEX	52	50	39	37
High-grade solution				
Composition (mg/L): Au (10), Zn (4), Ni (9), Co (0.5), Cu (10)				
CAPEX	23	38	23	14
OPEX	55	51	42	40

- The capital cost of the elution section of the MINRIP^{TM} process is less than that of CIP. The higher the tonnage, the more advantageous the MINRIP^{TM} process becomes.
- The capital cost of the adsorbent inventory of CIP is less than that of the MINRIP^{TM} process.
- The cost of the compressor to produce the air required for agitation and pumping constitutes a significant percentage of the equipment cost of the MINRIP^{TM} adsorption plant. Hence, if air is available, the capital cost of the MINRIP^{TM} plant would be reduced.

- The cost of the kiln to regenerate carbon constitutes a major portion of the equipment cost of the CIP plant.
- In general, the capital cost of a MINRIP^{TM} plant will be less than the cost of a CIP plant to treat tonnages of less than 150 kt/mo.

7. RECOVERY OF GOLD FROM PREG-ROBBING ORES

In the case of carbonaceous ores in which the bulk of the contained gold is available for direct cyanidation, carbon-in-leach (CIL) is generally applied for the recovery of gold with varying degrees of success, depending on the aggressiveness of the preg-robber. In cases where the activity of carbon is insufficient to compete effectively with the preg-robber, it is common practice to use CIL in conjunction with a blanking agent. However, the blanking agent, generally an organic reagent, does not only foul the carbonaceous preg-robber, but the activated carbon as well. Resins are less prone to organic fouling, and can be successfully used in the presence of some organic blanking agents.

Minix was evaluated for its capability to recover gold from preg-robbing ores (Lewis and Bouwer, 2000). Batch gold dissolution tests were performed on three ore samples originating from the same ore source. These included two run-of-mine (ROM A and B) ore samples and one flotation concentrate (FC) sample. Organic carbon content of these samples varied between 0.42% and 2.34%. Tests were done on direct cyanidation (CN), cyanidation in the presence of the adsorbent (RIL, CIL), and cyanidation in the presence of the adsorbent and a blanking agent (RIL + BA, CIL + BA). Results obtained are given in Fig. 8.

The results indicated that gold recovery can be very different for different ore sources, and that the gold recovery is not related to the carbon content of the ore, but rather to the aggressiveness of the preg-robber. RIL, in combination with a blanking agent (RIL + BA), was found to be beneficial in all three cases, enhancing gold recovery significantly.

The optimum adsorbent for a particular gold-recovery application is not necessarily the adsorbent that yields the highest gold loading, but rather the adsorbent that results in the most profitable operation. A preliminary economic evaluation comparing RIL and CIL was carried out for an operation located in West Africa, which treats 40 kt of preg-robbing ore per month. Process simulation and cost models were used to estimate the CAPEX and OPEX for conceptual RIL and CIL plants, and the results are shown in Fig. 9. Since pulp flowrate and gold dissolution determines the size of the leach/adsorption circuit, the CAPEX for this section of the circuit was

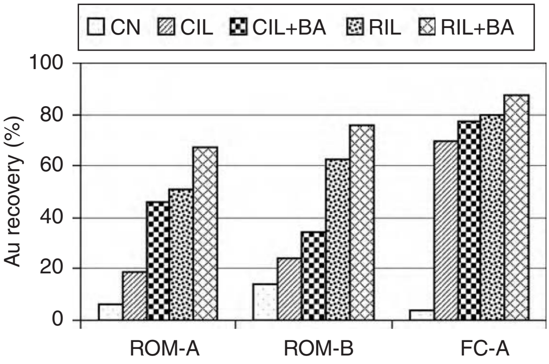

Fig. 8. Gold recovery during batch tests.

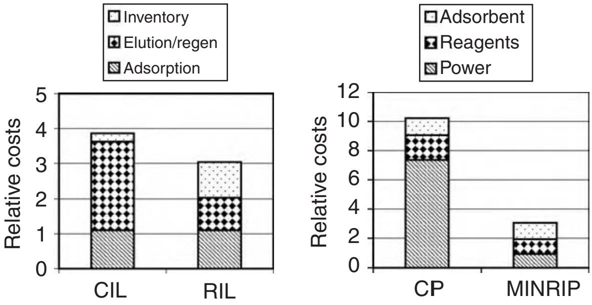

Fig. 9. Comparison of (a) CAPEX and (b) OPEX for CIL and RIL circuits.

assumed to be the same for both adsorbents. The flowrate of the adsorbent is dependent on its metallurgical response in the specific pulp and determines the adsorbent inventory, size of the elution facility, reagent consumption for stripping and adsorbent losses. The adsorbent flowrate was estimated using a process-simulation model with the equilibrium and kinetic response of the adsorbent in this specific pulp as input parameters.

The batch dissolution tests indicated gold recoveries of 80% and 87% for the CIL and RIL operations, respectively. Apart from the lower CAPEX and OPEX predicted for the RIL operation, higher revenues should also be realized as a result of the higher gold recovery. For other preg-robbing applications, the difference in gold recovery can be significantly higher in the favour of RIL.

It is, therefore, clear that RIL can be a more cost-effective technology than CIL for the recovery of gold from preg-robbing ores. The cost savings and additional revenue that can be realized by using RIL instead of CIL has to be quantified for each ore. Hence, a niche market exists for the use of the Minix resin for the recovery of gold from preg-robbing ores where the superiority of this resin over activated carbon has been demonstrated on an operating plant (Penjom) in Malaysia since September 1999 (Lewis, 2000). The use of this adsorbent in an RIL circuit has resulted in significant improvements in gold recovery when compared to the CIL and RIL (with a 'selective resin) technologies previously employed.

8. RESIN-IN-SOLUTION

As a result of a relatively depressed gold price, there is a worldwide trend towards low-cost heap-leaching operations. Heap leaching provides relatively low-grade, clear solutions from which gold has to be upgraded. Carbon-in-solution (CIS) is generally used for this purpose.

8.1. MINIX

After Mintek had completed developments of its RIP process and Minix resin, attention was given to the recovery of gold from clarified solutions with this resin (Van Deventer *et al.*, 1999).

Mintek and LTA Process Engineering (currently Grinaker LTA, South Africa) conducted a techno-economic evaluation to compare RIS, using Minix, and CIS for the recovery of gold from a typical heap-leach liquor. A lead-lag-lag (three columns in series) fixed-bed adsorption circuit was proposed for the recovery of gold from heap-leach liquors at a typical gold concentration of 1.5 mg/L. A residence time of 8 min was allowed for both adsorbents to decrease the gold of the feed to below 0.01 mg/L in the barren.

In order to minimize resin handling and associated resin losses, it was proposed that the resin elution be done in the same column as adsorption. A resin loss of 5% per annum was assumed. After adsorption, carbon has to be transferred to a separate elution column that can tolerate the relatively high temperature and pressure. The low cost of replacing carbon makes this more economical than to construct all the columns to comply with elution column specifications. Carbon loss was assumed at 0.02 g/t of ore treated.

For sizing of the full-scale plant that needs to treat 150 m^3/h of clarified pregnant liquor, it was assumed that the resin and carbon loadings would be similar in a typical heap-leach solution. Mintek sized the adsorption circuits for both Minix and carbon, which were similar based on the above assumption. LTA Process Engineering used this information to prepare a preliminary comparative costing for RIS and CIS plants. Summaries of the preliminary comparative CAPEX and OPEX for CIS and RIS plants are presented in Fig. 10. Maintenance of each plant was assumed at 5% of

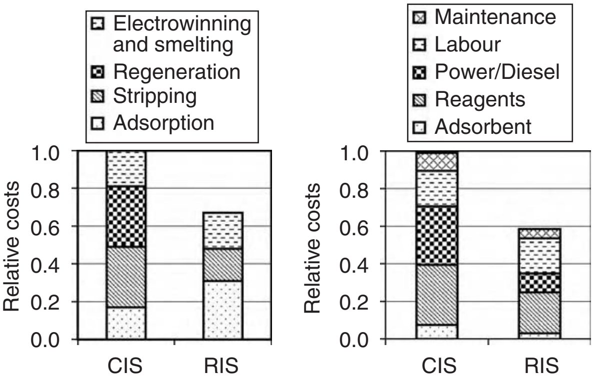

Fig. 10. Relative CAPEX (a) and OPEX (b) estimates for CIS and RIS.

CAPEX per annum. Labour and water requirements were assumed to be the same for both plants.

For this application it was estimated that the CAPEX for the RIS plant would be ~30% lower than that of a CIS plant. The main difference in the CAPEX for these two plants was the regeneration kiln required to regenerate activated carbon, while no thermal regeneration of the resin is required. It was estimated that the OPEX for RIS would be 40% lower than that of the equivalent CIS plant.

The preliminary techno-economic comparison between RIS, employing the Minix resin, and CIS indicated that major savings could be realized when RIS is employed for the recovery of gold from low-grade gold solutions such as heap-leach liquors.

8.2. AuRIX®

Lycopodium Pty Ltd of Perth, Western Australia carried out a financial evaluation of RIS vs. CIS using AuRIX® resin pilot-plant data (Fisher *et al.*, 2000). The key CIS and RIS design criteria used as a basis for the evaluation are summarized in Table 8. The adsorption-circuit design parameters are given in Table 9.

The capital and operating cost estimates were based on US dollars as of the first quarter of 1999 to an accuracy of ±25% for a facility located in the goldfields of Western Australia. No allowance was made for

- mining capital;
- heap-leach pad and pond construction;
- capital for ore crushing and stacking areas;
- power and water supply;
- royalties and license fees; and
- owner's costs.

Table 8
Summary of key CIS/RIS design criteria

Parameters	Units	Carbon-in-Solution circuit		Resin-in-Solution circuit	
		Case 1	Case 2	Case 3	Case 4
PLS[a] flowrate					
Nominal	m^3/h	400	100	400	100
Design	m^3/h	500	125	500	125
PLS grade					
Gold	mg/L	0.50	2.00	0.50	2.00
Silver	mg/L	0.05	0.20	0.05	0.20
PLS flow direction		Upflow	Upflow	Downflow	Downflow
Volumetric flowrate	BV/h	50	50	60	60
Specific velocity	m^3/m^{2}h	60	60	60	60
Number of contactors	no.	5	6	4	5
Design gold loading	g/t	1,250	5,000	4,000	10,000
Elution type		Pressure Zadra	Pressure Zadra	Atmospheric	Atmospheric
Elution batch size	t (dry)	5.0	1.2	2.89	0.72
	t (wet)			5.95	1.49
Elution frequency	d	1.3	1.3	2.3	1.5
Eluate flow direction		Upflow	Upflow	Upflow	Upflow
Elution cycle time	h	16	16	12	12
Number of electrowinning cells	no.	2	3	2	3
Configuration of cells		Parallel	Parallel	Parallel	Series
Size of cells	mm	800 × 800	800 × 800	800 × 800	800 × 800
Number of cathodes		12	12	12	12

[a] PLS – pregnant leach solution.

Capital costs were estimated for the adsorption, elution, gold room, regeneration, and reagent/services areas. The capital cost estimate for each circuit is summarized in Table 10. Operating costs were estimated for the adsorption, elution, gold room, regeneration and reagent/services area in terms of consumables, maintenance, labour and power. The operating cost estimate for each circuit is summarized in Table 10 as an overall operating cost and as the total operating cost per ounce of gold produced.

Table 9
Summary of adsorption circuit design parameters

Parameters	Units	Carbon-in-Solution circuit	Resin-in-Solution circuit
PLS Flow direction		Upflow	Downflow
Volumetric flowrate			
Design	BV/h	50	60
Specific velocity			
Design	m^3/m^2h	60	60
Bed expansion			
Nominal	%	23	—
Design	%	50	—
Number of contact stages			
High-grade PLS	no.	6	5
Low-grade PLS	no.	5	4
Target PLS gold grade			
Maximum	mg/L	0.05	0.05
Gold loading			
High-grade PLS	mg/L	5,000	10,000
Low-grade PLS	mg/L	1,250	4,000
Circuit residence time[a]			
High-Grade PLS	min	7.2	5.0
Low-Grade PLS	min	6.0	4.0

[a] Circuit residence time is based on static bed volume. The circuit residence time in expanded bed contactors is greater.

9. RIP PLANTS

9.1. Golden Jubilee Mine, South Africa

In 1988, the Golden Jubilee Mine converted their CIL operation to RIP employing a conventional strong-base resin (Duolite A161L), as no gold-selective resins were commercially available at the time. Because in this case a CIL plant was replaced by a RIP plant, the two processes could be compared directly. Comparative performance of the two processes is given in Table 11 (Fleming, 1993). The resin loss was estimated at 10 g/t, which is about that expected of this resin type, according to the results of large-scale work done by Mintek.

9.2. Penjom Gold Mine, Malaysia

Penjom Gold Mine is Malaysia's largest gold producer and is located in the state of Pahang. The gold-processing plant treats around 600,000 tpa of ore from an open-pit mine. Typical head feed grades to the plant average between 6 and 10 g/t. However, organic carbon levels in this ore generally range between 0.2 and 1.5%, which causes a severe preg-robbing problem. Tests

Table 10
Capital and operating cost estimate[a] for RIS vs CIS using AuRIX®

Cost centre	CIS circuit		RIS circuit	
	Low[b] US$ (000's)	High[c] US$ (000's)	Low US $ (000's)	High US $ (000's)
Direct costs				
Adsorption	317	229	323	189
Elution/gold room	629	349	410	287
Regeneration	302	221	0	0
Reagent/services	379	284	263	221
Total direct	1,627	1,083	996	697
Indirect costs				
EPCM	250	250	250	250
Preproduction	71	71	68	68
First fill[d]	182	83	877	326
Working capital	244	152	165	117
Spares	45	30	30	20
Insurances	8	5	5	4
Total indirect	800	591	1,395	785
Contingency	238	155	173	113
Grand total	2,665	1,829	2,564	1,799

[a] (±25%, US$, 1Q99).
[b] 'Low' refers to low-grade PLS (0.5 mg Au/L at 400 m^3/h).
[c] 'High' refers to high-grade PLS (2.0 mg Au/L at 100 m^3/h).
[d] Resin cost = US $30.00/wet kg, Carbon cost = US$2.29/kg.

Table 11
Comparative performance of CIL and RIP at Golden Jubilee Mine

Parameter	Units	CIL plant	RIP plant
Plant capacity	Tpd	250	450
Gold grade	g/t	1.0–1.5	1.0–1.5
Liquid/solid ratio in leach		1.5	1.5
Number of adsorption stages		4	5
Size of adsorption tanks	m^3	60	10
Adsorbent inventory	t	2.4	1.0
Adsorbent loading	g/t	800–1,500	4,000–6,000
Adsorbent flowrate	kg/d	200	120
Gold in tails	g/t	0.2–0.3	0.10–0.15
Gold in solution tails	mg/L	0.1–0.3	0.02–0.05
Overall gold recovery	%	60–70	85–90

undertaken by Mintek have confirmed that Penjom ore is one of the most preg-robbing ores known in the gold industry today (Lewis, 2000).

At Penjom, the CIL circuit was converted to an RIL circuit owing to the preg-robbing nature of the ore and the poor recoveries obtained with carbon. A conventional strong-base resin was then used to replace the carbon, but due to the poor selectivity of this resin for gold, base-metal loading was high. This resulted in a large resin flowrate, with depressed gold loadings. At this stage the Minix resin became commercially available, and the plant was converted to use Minix as this resin had been demonstrated to have good selectivity for gold over the base metals in the plant liquor. Resin losses of the Minix resin was claimed to be below 5 g/t on this plant.

Lewis (2000) reported that from the operating experience at Penjom, resins are an appropriate choice for the treatment of carbonaceous ores. Resin is virtually unaffected by the addition of hydrocarbons, whereas activated carbon can be difficult to regenerate after exposure to either kerosene or diesel. There is also a safety risk in attempting to elevate regeneration temperatures to eliminate the hydrocarbons. Lewis further reported that regeneration of Minix resin is simple and gold can be consistently removed down to concentrations of 50 g/t. There are significant cost savings in resin stripping of Minix compared with the costs of stripping and regeneration of activated carbon.

9.3. Muruntau, Uzbekistan

The Muruntau operation (McQuiston and Shoemaker, 1981) was claimed to be the largest of over 20 RIP/RIL plants in the CIS, and amongst the lowest cost producers. It treated over 1.3 million tons of ore per month at an average gold grade of 5 g/t, producing about 70 t of gold per annum. These plants employ air-agitated tanks, and internal airlifts for resin and pulp transportation. Resin/pulp separation is effected by the use of externally mounted stainless-steel woven-mesh screens (aperture of 0.5 mm). The AM2B resin is used; the elution of this resin has been described earlier in this chapter.

9.4. Barbrook Gold Mine, South Africa

During 2002, the Barbrook Gold Mine implemented RIL, using Minix, for the recovery of gold from a preg-robbing ore (Anonymous, 2003). However, there is very little operational information available regarding this plant. Kemix Anglo American Corporation (AAC) pump cells are being used as the contactors in the adsorption circuit.

10. CONCLUSIONS

This chapter has given a brief overview of the development of anion-exchange resins for the recovery of gold cyanide from cyanide leach liquors in RIP, RIL and RIS circuits. At least three gold-selective anion-exchange resins are currently available commercially, namely Minix, AuRIX® and AM2B.

When CIP was introduced as a new technology for the recovery of gold, it was initially demonstrated on tailings. Once it was successfully demonstrated for gold recovery and confirmed its potential advantages over the earlier Merrill-Crowe operations, it was widely accepted in the industry. It is envisaged that RIP would probably follow a similar introduction into the gold-mining industry, where it will initially be slowly introduced on plants where CIP is problematic (*e.g.*, preg-robbing ores), and then it could become more acceptable for general implementation.

RIP has also demonstrated, during laboratory and plant evaluations, to be a stronger adsorbent for the recovery of gold from preg-robbing ores, and that recoveries of gold could be improved when RIL is used instead of CIL. This aspect, together with the fact that resin is stripped at relatively low temperatures and pressures and does not require thermal regeneration, would potentially make the RIL circuit significantly more profitable than CIL.

Resin losses have always been a concern, as resins are more expensive than carbon. However, the resin losses quoted by Penjom Gold Mine (which agrees well with the resin loss prediction by Mintek for this resin) confirms that resin losses could be an order of magnitude lower than that of carbon.

Given all the advantages of resin as demonstrated in the discussion in this chapter, and the fact that resins are commercially available, the commercial success and acceptance of the RIP/RIL/RIS process in the gold industry will probably be determined in the next decade.

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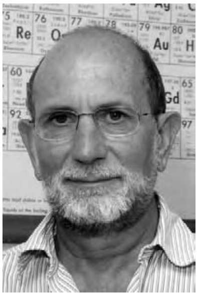

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Mike Virnig, after receiving a PhD in organic chemistry with a minor in inorganic chemistry from Iowa State University, Michael joined General Mills Chemicals in 1973 as a research chemist working on the identification and development of new metal extractants. General Mills Chemicals was purchased by Henkel in 1977. In 1999, Henkel separated out its chemical business and set it up as Cognis Corporation. From 1973 to the present, over some 30+ years, Michael has been part of the Mining Chemicals Technology group of Cognis, involved in the development of new reagents, manufacturing processes for extractants, new applications for metal solvent extraction reagents and solutions to customer problems. Michael is currently the Director of Technology for the Mining Chemicals Technology business, responsible for its R&D programs and technical service. He is listed as an inventor or co-inventor on more than 50 US patents and has authored/co-authored over 20 technical papers.

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Chapter 26

Electrowinning

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1. BACKGROUND

Electrowinning is most often used to recover gold and silver from eluates produced by the elution of activated carbon. Operation of the electrowinning process differs depending on the elution procedure that is used. In the case of Zadra elution, where the electrowinning cell is in series with the elution column, the column and cell must be designed to elute and recover the gold by re-circulation of the eluant until the gold content of the eluted carbon is low enough (<100 g/t) to be reactivated and returned to the adsorption circuit.

In the case of Anglo American Research Laboratories (AARL) elution, electrowinning is carried out on the complete batch of eluate produced by a single pass through the elution column. The pregnant eluate is re-circulated through the cell until the concentration of the gold in the barren solution is low enough to be discarded or returned to the adsorption circuit. The cell is operated independently of the elution process.

The reactions occurring at the electrodes of a cell recovering gold from eluates containing cyanide and/or alkali are:

Cathode:

$$Au(CN)_2^- + e \rightarrow Au + 2CN^- \tag{1}$$

$$2H_2O + 2e \rightarrow H_2 + 2OH^- \tag{2}$$

$$O_2 + 2H_2O + 4e \rightarrow 4OH^- \tag{3}$$

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Anode:

$$4OH^- \rightarrow O_2 + 2H_2O + 4e \tag{4}$$

Oxygen has a limited solubility in solution, so the partial current for the reaction depicted in Eq. (3) is generally a small fraction of the overall current. For most of the electrowinning cycle the gold and silver concentrations in the cell are comparatively low, so the partial current due to reaction (1) is much smaller than that due to reaction (2) so that for most of the cycle, reactions (2) and (4) predominate.

The maximum rate of deposition of gold (*i.e.* of depletion of gold from the solution), is given by the mass-transport controlled rate of deposition:

$$-\mathrm{d}C/\mathrm{d}t = kAC/V \tag{5}$$

where k is the mass-transfer coefficient (cm/s), V the cell volume, C the gold concentration and A the cathode area.

Integrating, this becomes

$$C = C_0 \exp(-kAt/V) \tag{6}$$

where C_0 is the initial gold concentration.

Deposition of a metal onto a packed-bed electrode at a rate controlled by mass transport is given by

$$C = C_{\mathrm{o}} \exp(-L/\lambda) = C_{\mathrm{o}}(1 - E) \tag{7}$$

where C_{o} is the inlet concentration, C the outlet concentration, L the thickness of the bed in the direction of solution flow, λ the *characteristic length* of the cell and E the *single-pass extraction* of the cell.

λ is an experimentally determined parameter which is characteristic of a particular bed and which varies with the flowrate ($\lambda = kU^{0.5}$, where U is the linear flowrate).

The decay of gold concentration with time for electrowinning a batch of eluate by recirculation at a volumetric flowrate U_{v} is described by

$$C_{\mathrm{t}} = C_{\mathrm{I}} \exp\{-U_{\mathrm{v}}(1 - \exp(-L/\lambda)t/V\} = C_{\mathrm{I}} \exp(-U_{\mathrm{v}}Et/V) \tag{8}$$

where C_{I} is the initial concentration and C_{t} the concentration after time t.

By determining λ, the total cathode thickness (L) required to achieve a particular recovery in a given time and flowrate can be calculated.

The single-pass extraction efficiency (E) is relatively constant throughout the elution cycle and an average value of $E = 0.9$ has been found to be typical of cells operated with the Zadra elution owing to the high solution conductivity ($>8\,\mathrm{S\,m^{-1}}$) and high eluate temperatures (80°C). When the AARL elution is used, both the solution conductivity ($2\,\mathrm{S\,m^{-1}}$) and the temperature (30–50°C) are much lower, resulting in higher λ values for the AARL process.

The actual operating current required (typically ~400 A m^{-2} of cell cross-sectional area) depends on a number of factors such as the flowrate, maximum gold and silver concentration and temperature. The cell voltage (generally ~3–10 V) depends mainly on the anode–cathode spacing and the solution conductivity.

The evolution of oxygen at the anode by the reaction depicted in Eq. (9) results in a decrease in the pH at the surface of the anode:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e \tag{9}$$

If poorly controlled, the pH value can decrease to the point where corrosion of the anode occurs, by anodic oxidation of the chromium in the stainless steel to chromate, which can then be reduced to a chromium hydroxide on the steel wool cathodes via reaction (10):

$$CrO_4^{2-} + 4H_2O + 3e \rightarrow Cr(OH)_3 + 5OH^- \tag{10}$$

This electrodeposited layer of chromium on the cathode has been shown to inhibit the deposition of gold and catalyse the evolution of hydrogen, reducing electrowinning efficiency. It is recommended that the pH of the solution be maintained above 12.5 to avoid this problem, which is more when the AARL elution procedure is used.

2. HISTORICAL DEVELOPMENTS

One of the earliest references to gold electrowinning was contained in British Patent 9582 (1842), in which William Henry Fox Talbot described a method for plating gold using metal electrodes in an electrolyte and powered by a galvanic cell. This summary will try to record some of the practical aspects learned over the last 160 years of experience available in this field.

The advent of the use of coconut-shell-based activated carbon to recover gold from cyanide solutions (see Chapter 23), and the need to recover the gold from pregnant eluate solutions resulting from elution of the loaded carbon led to the adoption of electrowinning as the primary means of gold metal recovery. The basic design features of the electrowinning step were published by the United States Bureau of Mines (USBM; Zadra, 1950). The paper described the elution conditions necessary for both closed recirculating systems and open-pass systems; however, the former was adopted as the standard procedure, and the electrowinning cell described was intended for use in a closed recirculating system.

This type of cells were to some extent limited by stationary diffusion layers developing adjacent to the plating site, which inhibited the transfer of the plating ion across the barrier, and to the thickness of the packed bed.

Britton (1963) described a tangentially agitated high current–density silver-recovery cell. This cell featured a cylindrical anode–cathode enclosure, in which the electrolyte was introduced tangentially at the bottom of the cell, and spiraled through an annulus to leave tangentially at the top of the cell. There is now over 40 years of experience with this type of cell.

3. ELECTROWINNING CELL DESIGN

3.1. Early designs

The USBM design was based on a cylindrical packed bed of steel wool as cathode. The electrolyte was introduced to the centre of the cell and flowed through the packed bed and out of the top of the cell. The anode was a cylinder of punched-plate or mesh stainless steel located around the cell's outer circumference.

Either a single cell or multiple cells in a series cascade arrangement could be used. The total system operated at atmospheric boiling point for the particular elevation and electrolyte composition at the site and was usually operated in the range 95–99°C.

The elution rate of the gold from the carbon in to the eluate was limited by the relatively low temperature and due to the cell inefficiency, gold which was not plated was recycled to the carbon, further inhibiting the elution rate.

These two effects resulted in elution cycle times in the range 24–96 h. This was a serious problem for operators, who needed to turn their carbon over much more quickly. Means were therefore sought to speed up both the elution and electrowinning processes.

In some instances, custom elution contractors would toll charge for elution on a time basis, resulting in the return of poorly eluted carbon to the adsorption circuit.

Attempts were made to increase the mass transfer and plating rates in cylindrical cells by instituting pumped internal recirculation; however, this technique failed to generate the required increase in efficiency.

3.2. Cell types in use in Australia

In 1998, a cooperative effort between a consultant engineer and the West Australian Chemistry Centre and Commonwealth Scientific and Industrial Research Organisation (CSIRO) led to the design and construction of a tangentially agitated annular electrowinning cell. Trials with the cell revealed two serious problems. The first was there was no practical way to provide the plating surface area that the steel-wool-based cathodes provided, and the cells became too long, or required too many units in series. The second was that if the annular gap was reduced to obtain high surface turbulence and high mass-transfer rates, the gold plated was either too fine or too colloidal, and travelled out of the cell with the electrolyte. The idea was abandoned and further improvements were directed to parallel-plate cell designs featuring multiple cathodes.

It is interesting to note that this type of cell design was progressed, and is now in commercial operation in the copper industry, and has been piloted for commercial operation in the silver heap-leach industry. The author has no knowledge of these cell designs finding application in gold elution and electrowinning circuits.

3.3. Cells for pressurized elution circuits

The need to electrowin in 10–16 h resulted in the implementation of pressurized elution circuits, which demonstrated faster elution kinetics than atmospheric systems. Some of the earliest designs of pressurized elution circuits in Australia occurred in the early 1980s (North Kalgoorlie Mines Limited, Kambalda), and featured elution temperatures in excess of 100°C. Under these conditions the elution rate was very much faster; hence, the electrowinning rate was also required to be faster.

In addition to the increased operating temperature, there were several other variations that impacted on the design of the required electrowinning system. These were

- The *Pressure Zadra* system, in which the circuit was closed, the gold was presented to the cell in pulse form, and it was critical not to return gold to the carbon still in circuit in the column.
- The *Open-circuit AARL* (Anglo American Research Laboratories) system, in which the circuit is left open and no re-use of the second half of the eluate volume in the next cycle is practiced.
- The *Split AARL (SAARL)* system, in which the circuit is partially closed, with the first half of the eluate volume proceeding to electrowinning, and re-use of the second half is practiced.

Within these sub-groups it was generally accepted that for the Pressure Zadra system the electrowinning cells must accept the flow equivalent to a flow rate in the range 2–5 carbon volumes per hour, with 2 or 3 being the most common selection. For the two variations of the AARL system, it was generally accepted that electrowinning needed to be completed within 16 h if a single elution cycle was to be completed in one day, or in less than 10 h if two elution cycles were to be completed in one day.

As a further possible variation in the AARL systems, the designer may elect to use recirculation of the electrolyte for the required time to reach a design barren-electrolyte grade, or he may elect to design for a system that will generate an acceptable barren-electrolyte grade in a single pass. It may also be found that a combination of these with either partial recirculation followed by open-circuit pass out, or multiple open-circuit passes without mixing and recirculation achieves the lowest barren in the available time with the least number of cells.

3.4. Cathode design

3.4.1. Multiple-cathode parallel-plate electrowinning cells

Increases in electrowinning cell performance and efficiency was achieved by replacing the single cylindrical packed-bed cathodes, used in the original US Bureau of Mines (USBM) designs, with multiple rectangular parallel-plate cells. The packed-bed feature was still retained, and steel wool was packed into the cathode enclosure, with electrical contact achieved via a stainless-steel spike entering vertically from the surface.

These cells suffered from the effect that as the electrolyte flowed through the bed, it entered the area that was below the deposition potential of gold, owing to the resistance drop through the electrolyte and the loosely packed steel wool. Individual cathode-pass efficiencies per unit weight of cathode were low.

A further disadvantage was the need to process large masses of residual steel wool, usually by dissolution in hydrochloric acid. This process was relatively difficult, being labour intensive and unhygienic; it was not unusual at the smaller operations to see a plastic rubbish bin of gold/steel-wool sludge sitting outside the gold room in the sunshine and fresh air, being given the occasional stir with a broom handle.

3.4.2. Wound single-layer wrapped cathodes

There was a developing tendency to change to rolls of steel wool and wind these on to a high-density polyethylene (HDPE) cathode former. The winding method was to overlap each strand by 30–50% and to cross wrap a second layer at right angles, with winding densities on the order of 2,000 g/m^2 being typical. Skilled gold-room operators, always with an eye to reducing their workload, progressively reduced the winding density, until the cell-pass efficiency was compromised. This process continued until the standard cell winding density was on the order of 1,000 g/m^2.

The required number of such cathodes in series that was required to achieve a target single-cathode pass efficiency, and hence a target cell pass efficiency, was calculated after examination of site operating data.

The practice of sub-contracting cathode construction to disabled people was also initiated. The operator was saved the time of winding his cathodes and the supplier performed a very useful service to the gold industry. Cathode-enclosure designs were changed to accommodate these pre-formed cathodes and clamp them to a transverse copper conductor bar using a plastic pressure-plate as part of the cathode enclosure. This cell design using nine cathodes and ten anodes became the workhorse of the Australian gold industry. A typical cell operating at good efficiency would plate 70% of the gold in a single pass, with poor operations as low as 40% and the best operators achieving 90% pass efficiencies.

In South Africa, the Mintek cell, featuring six cathodes in series, and fabricated from stainless steel was chosen as the standard cell.

The advent of corrosion at the solution interface, and breaking off of the cathodes at the surface was a serious problem. When the cell is in service the relatively fragile steel-wool wires are cathodically protected by the applied current and cannot corrode. Between cycles the reverse occurs, and the moist area at the solution interface anodically corrodes. Anode wires also corrode and thin out at the base, causing excess current density at the surface. The steel wool is also inflammable, and can contribute to cell fires. Some designers countered this problem by dropping the transverse bus bar to the surface, and eliminating the non-wetted wire. Others developed a saw-tooth cathode former and wound the wool horizontally so that it was always immersed.

3.4.3. Woven stainless-steel cathodes – plate and replate cells

Barnes and Raponi (1991) published data on the use of woven stainless-steel cathodes to electrowin gold. The loaded cathodes were then transferred to a replate cell, in which the polarity was reversed, the plated gold was anodically corroded and replated on to a plain polished stainless-steel cathode plate. The operator then scraped the metallic foil from the plates and smelted it to bars. The system worked reasonably well and was selected for use by one of the major producers at that time, the Telfer gold mine in Western Australia.

There were several features of the system that were beneficial. It was observed that as the replacement cell was started the gold dissolution rate was anode current-controlled as a result of the high surface area of the original woven stainless-steel cathodes. Gold in solution tenors therefore increased rapidly. The replate plating reaction started slowly, owing to low grades in solution, but then increased as the bulk solution tenor increased. The net effect was that plating would plateau at approximately 3,000 g/m^3 Au, and continue at that level until the anodes were depleted in gold.

If copper had been electrowon on to the original cathodes, it would also anodically dissolve; however, by manipulation of the free cyanide level in the cell, the copper could be maintained in solution, and replating of copper did not occur. The cells therefore had some electrorefining ability and became known as electrorefining cells.

There were other disadvantages of the system that arose; for example, sometimes it was very difficult to remove the plate. In circuits using closed-circuit elution, where the carbon was contaminated with silicate minerals, the silica dissolved in the hot caustic eluant at the high-temperature section of the circuit, and reprecipitated in the cell at the coolest part of the circuit. The stainless-steel cathode wires became coated and the cell resistance became so high that it could not meet its design duty.

There was therefore a need to develop a system to delete the replate step and to pressure jet the bullion off the woven stainless-steel cathodes directly.

3.5. Pressure-cleaned systems for stainless-steel cathodes

3.5.1. Pressure-jetting bullion-sludge removal

Barnes and Raponi (1991) had also published data on the elimination of the replate stage and the practice of using a high-pressure water jet to directly remove the bullion as a sludge. The recommendation was to plate at very low current densities of less than 5 A/m^2, with the aim of plating poorly attached, easily removable gold.

Several operators of replate circuits converted to the pressure-cleaning system, usually with success. In 1995, the decision was taken to expand the Fimiston complex in Kalgoorlie, Western Australia and to convert from the conventional steel-wool cathodes to woven stainless-steel with an all-sludge bullion-handling system.

Fimiston was unusual in that it produced carbon loadings of greater than 15,000 g/t from the calcine circuit, and carbon loadings of less than 500 g/t from the float tail circuit; hence the electrowinning gold head grades could be as low as 45 mg/L or as high as 500 mg/L. A major testwork programme was set up using actual plant eluates and a pilot electrowinning cell. The relationship between plating current density, solution head grade, linear velocity, and degree of plate attachment was developed. An additional variable was the trade off between increasing efficiency of increasing numbers of layers of woven stainless-steel cathode, and increasing difficulty of removal due to the outer layers shielding the inner layers.

Micrographs were also used to show the type of plate occurring and the degree of attachment still remaining as carryover after a chosen cleaning procedure. The data clearly showed that for high-grade solutions, competent gold metal was so strongly attached that only the most robust industrial cleaners could achieve removal, and nozzle pressures of 20,000 kPa were required. Collateral damage to the cathode wires and support structure was a design consideration.

Access between anode and cathodes for the high-pressure cleaning nozzle was a further problem, which at that time was not resolved, and a separate wash station was provided.

The system was carried forward to the production stage and all of the Big Pit gold production is now produced through four 24-cathode 1 m^2 cells operating at currents of approximately 3,500 A cell.

3.5.2. Gangued cathode and anode arrays

In 1999, the new concept of arranging the anodes and cathodes in a rigid array was introduced at the Pajingo mine in Queensland. This idea had several advantages. All connections were rigidly bolted and there was little possibility of poor connections and uneven current and voltage distribution. The removal of the anode array prior to pressure cleaning the cathodes provided space for insertion of the cleaning head, and the cathode array could be slowly lifted to gain access to the lower sections of the individual cathodes. The system has found wide acceptance and is routinely selected for large installations.

3.6. Ultrasonic bullion removal

In the early 2000s, Delkor Limited of South Africa announced their intention to develop an electrowinning cell, in which the gold was conventionally electrowon onto woven stainless steel in one compartment, and then ultrasonic bullion removal was completed in another, with the cells operating in a continuous carousel mode.

The development project did not succeed and was discontinued.

3.7. Pressurized electrowinning cells

In the mid-1980s, the concept of operating closed-circuit elution circuits without intermediate heat-exchange to cool the eluate to less than atmospheric boiling point was introduced. The electrowinning cell was enclosed in a pressure vessel and for the first time electrowinning at temperatures of 130–140°C was practiced. The design was known as the *Integral Pressure-Strip Electrowin Cell*. Oxygen solubility was expected to be zero and high current efficiencies were expected.

The units were developed as containerized, transportable pre-commissioned units and were adopted in many countries with remote sites, and many in Australia. They are responsible for significant gold production and have found continuous application. The units suffered from the disadvantages of all stainless-steel construction described above, and owing to the fact that they operated under pressure, the operator had no access to on-line current and voltage measurement or troubleshooting.

As elution column sizes increased, the practice of operating at high linear velocities was also used to achieve the flow necessary in the same cross-section cell, with entry to the centre of the cell and split exits from each end. This caused some operations to experience severe sludging problems, with bullion sludge deposition in the outlet end of the cell, and anode–cathode pair short-circuiting occurring.

3.8. Rotating-cathode electrowinning cells with in-cell pressure bullion removal

In the early 2000s, Kemix Pty Ltd in South Africa introduced the concept of an electrowinning cell enclosed in a cylinder (the Kemix Sludge Reactor). The unit features a rotating cathode where gold sludges form and built-in high-pressure cathode wash jets that wash off all the gold in ~10 min. Higher flowrates and a greater number of passes are used to achieve a similar result to more conventional flowrates and high pass efficiencies.

On completion of the electrowinning cycle the cell changes to the cleaning cycle, and the bullion is flushed out of the bottom of the enclosure to a holding tank for final processing.

There are three plants using this system in South Africa. Kloof gold mine produces three tonnes of gold per month, all of the gold being sludged in a system with seven sludge reactors. It is considered more suitable for plants that produce large amounts of gold.

4. SPECIAL APPLICATIONS

4.1. Electrowinning from gravity concentrates

In 1996, Gekko Systems of Ballarat in Australia piloted the concept of direct electrowinning of gold from intensively cyanided gravity concentrates. The idea was successful and has found routine use in the gold industry. The electrowinning is completed at ambient temperature, as opposed to AARL eluates, which typically operate at 50–60°C, Zadra eluates (95–99°C) and pressurized cells (130–140°C). The operational data allowed some evaluation of the effect of temperature. Even very low temperatures were piloted, when electrowinning in areas where the outside ambient was −40°C was contemplated. Design data based on actual operating data are therefore available covering the range 25–140°C, and pilot data are available down to 5°C.

Intensive cyanidation of concentrates may result in the dissolution of other species that can affect the electrowinning process, and in some cases could prevent electrowinning from occurring.

4.2. Direct electrowinning from biologically oxidized filtered leach solutions

Some designers of bio-oxidation plants choose to complete a solid/liquid separation on the oxidized, cyanided concentrate, and to use zinc precipitation as the final method of bullion recovery. The grades and solution flowrates are directly applicable to common sizes of electrowinning cells.

In one case, a production electrowinning cell was fitted to such a circuit to test the concept of replacing the entire Merrill–Crowe circuit by a direct electrowinning system. The data indicated that other species in the electrolyte solution were severely affecting cell performance, and the cell could therefore not meet the duty.

5. KEY ASPECTS OF ELECTROWINNING CELL DESIGN AND OPERATION

While not exhaustive, the following aspects are considered key to the design and operation of electrowinning circuits in gold plants.

5.1. Gold to steel-wool loading ratio

Experience has shown that a cathode wound to a density of approximately 1,000 g/m^2 can accept up to 20 times its weight of gold. As the gold loading increases, however, two changes occur – the available high surface area decreases and the cathode becomes impervious to hydraulic flow. Bypass of the electrolyte over the top, around the sides, and under the bottom of the cathode will occur, resulting in a significant loss of efficiency and limiting loadings to approximately five times the steel wool mass.

5.2. Limiting linear velocity

If the linear velocity is too low, the transport rate of gold to the plating surface will be too slow, and hence, the plating rate too slow. If gold is not presented at a fast enough rate to the cathode surface a second reaction will start and poorly attached powdery gold or colloidal gold will result. If the linear velocity is too high, the hydraulic turbulence has two effects – the gold may be physically abraded off the steel wool, or the cathode may start to oscillate hydraulically and break off at the surface connection to the transverse bus bar.

5.3. Cell flowrate and required cross-sectional area

The elution method chosen will fix the required cell flowrate and number of cells. The limiting linear velocity will fix the cell cross-sectional area. Physical handling characteristics constrain the upper size limit to approximately 1 m^2.

5.4. Current requirements

The total current required can be calculated from Coulomb's law, as can the known mass of metal, or metals, to be plated and the design available plating time. The current efficiency to be used in this calculation will vary greatly with metal concentration. Both pilot-scale laboratory experiments and plant data have been used to generate a relationship between metal grade and plating current efficiencies, and this relationship is used to decide the current efficiency applicable to a particular design and duty. Other reactions occurring in the cell, such as the reversible hydroxide to oxygen reaction Eq. (3), and the oxidation of cyanide to cyanate, will always carry a significant amount of the applied current. The entire performance of the system can be applied-current limited if allowance is not made for these effects, particularly if silver, which has a low chemical-equivalent mass, is present in significant amounts.

5.5. Current-density limitations

In addition to the manner of wrapping cathodes and the wrapping density, the operator typically has a choice from the suppliers of three types of steel wool and one type of woven stainless-steel mesh. The steel-wool grades are classified as grade zero, grade one, or grade three. Electron microscopy has been used to measure the wire diameters of these grades and hence, to calculate the surface area to mass relationship and actual plating current density. Double-woven stainless steel has been found to have a significantly lower surface area to mass ratio.

Current densities that are too low will possibly be below the deposition potential for gold, and no plating will occur. Current densities that are too high will result in poorly plated gold and co-deposition of other species, including the production of hydrogen gas.

5.6. Impact of type of elution system

As discussed above, the choice of elution system will impact on the concentration and volume of the eluate. Zadra systems will generate a pulse of metal of variable feed concentration. Open-circuit AARL systems will generate 7–8 bed volumes of eluate, which will mix by recirculation to a relatively steady head grade. Split AARL systems will concentrate the gold at higher concentrations into a smaller volume of approximately 5 bed volumes, and will therefore electrowin more efficiently.

5.7. Number of cathodes required

The number of cathodes required to achieve a particular cell-pass efficiency could be predicted theoretically, but as more and more operating data became available it was better to use this data as a practical model. In some designs, cells were built as single units containing 18 cathodes in a single enclosure, and other designs feature cascade arrangements of three standard 9-cathode cells in series, to effectively have a 27-cathode cell. For the major gold producers, for example Fimiston in Western Australia, very large cells were designed and built using 24 cathodes in series, and equipped with 5,000 A rectifiers.

5.8. Solution by-pass

It would seem to be a basic requirement that a cell design should require the eluate to flow through steel wool for plating to occur. Several designs either provide clearance under the cathodes, or around the cathodes, or run at a higher flowrate than the flow-through characteristics of the cathode can accept. There is a trade-off between maintaining pass efficiency and faster throughput, and hence more passes; however, a good design should attempt to satisfy both requirements.

5.9. Plate attachment and the role of silver and copper

When an operator lifts a freshly wound cathode after the first 30 min of the plating cycle, pristine yellow metallic gold is visible. Conversely, at the end of the plating cycle a dirty black powdery plate is observed. Clearly, one can plate well-attached metal from high-grade solutions ($>100\,\mathrm{g/m^3}$) but poorly attached powdery plate from low-grade solutions ($<5\,\mathrm{g/m^3}$) and the plate quality will vary across the range. When the next plating cycle starts the good plate has the last cycle's poor plate as a foundation. Successive plate attachment becomes successively worse, until in the worst case, sludging occurs and the bullion sludge may fall into the bottom of the cathode enclosure, if there is one, or, into the bottom of the cell.

If silver is present, a non-metallic electrum enriched in silver will deposit. Plate attachment is poor and if a hose-off system is in use, a simple garden-hose nozzle will detach the plate. Our old favorite, lead nitrate can be used to modify the attachment of the primary plate, making the whole assembly easier to remove.

Conversely, if copper enters the process (often undetected, as it will not be routinely monitored), the copper–gold alloys may be so massive and well attached that plate removal becomes almost impossible.

5.10. Electrical connections (resistivity, material selection and fire)

Initially, in Australia at least, cells were fabricated from HDPE. The material had adequate mechanical strength at high temperatures, was a non-conductor, and did not corrode. Unfortunately it had one very serious fault, it was combustible. For convenience, designers selected quick-fit compression clips to carry the current from a hard-wired copper side-bus bar to the copper transverse bus bar. These were required to be kept clean to ensure that no high-resistance joints developed. Unfortunately, for a variety of reasons this did not occur. The copper used is subjected to a continuous atmosphere of steam, cyanide mist and ammonia, so corrosion and film build-up is inevitable.

Major gold producers in Australia and Africa experienced cell fires, and in the worst instance total destruction of the entire gold room occurred and gold production stopped. The alternative was to use hard-wired connections, and this was initiated especially for anodes, which did not require removal of every cycle. A second alternative that was adopted by some designers was to change from copper to stainless steel. The very significant difference in electrical conductivity was neither appreciated nor allowed for. In one application, surveys carried out on cells using stainless steel indicated that the voltage drop down the main bus bar was so significant that the last electrode pair in the series was supplied with 56% less current than the electrode pair at the inlet end of the cell and there was a linear reduction in the cathode current from the inlet to the outlet end.

In another cell with copper main bus bars, and stainless-steel cross bus bars and droppers, individual dropper current measurement demonstrated that 47% of the current was flowing down the closest dropper, 32% down the central dropper, and 21% down the dropper on the anode bus side of the cell. When the voltage drop-down of the cathode wires themselves was added in to the calculation, the remote quartile of the cathodes were initially inactive. Gold is, however, a very good conductor, and after initial plate build-up, the effect of the resistance of the cathode wires is minimized. Woven stainless steel has different directional resistance properties and this feature needs to be allowed for in design.

There is an additional effect that occurs when defective connections occur. The cell operator only knows that he needs a target current to plate his gold in the time allowed. Unless he is monitoring individual electrode currents (despite the ease of this operation using a hand-held tong tester, very few operators do), he will be unaware that he has lost connection and several electrodes will be inactive. The applied cell-voltage is increased to achieve the target total current. The already heated high-resistance joints are further heated, and the well-connected cathodes are forced over their design limit and also begin to heat. Destructive cell fires are the result; in Africa during one after-hours incident, the operators present on site had no authority to enter the gold room and were forced to watch the cell burn on the security closed-circuit television (CCTV).

5.11. Automatic current-control rectifiers

An electrowinning cell is effectively a direct-current resistance unit. One of the current carriers is the gold-deposition reaction. At the beginning of the plating cycle when the gold solution tenors are high, maximum current is needed to plate the gold. As the gold plates, with removal from the solution phase, the cell resistance will rise and the current will fall. This is in keeping with the need to plate gold at a slower rate in the latter part of the plating cycle. Some designers have supplied automatic current control and forced the current to increase under conditions of depleted gold tenors. This should be a retrograde step and will force other side reactions to occur, resulting in increased anode corrosion. It is recommended that once the input current and voltage are decided and set, the current be allowed to fall and naturally follow the solution resistivity.

It may be that the use of stainless-steel side bus bars could have a beneficial effect. With a correctly chosen cross-sectional area, those cathodes doing most of the plating, at the inlet end of the cell, would receive more current than those at the outlet end, where plating is essentially completed.

5.12. Health hazards

As a result of the security requirements in gold rooms the building enclosures tend to be airtight and relatively compact. The cells operate at high temperatures and the open cell designs discharge a fume of steam, cyanide mist and ammonia from the surface. It is critical to provide adequate ventilation and it is recommended that all emissions be captured in a scrubber.

A well-designed installation will allow for safe access to the cell under operational conditions to allow the operator to monitor the electrical characteristics of the cell while it is on-line, and carry out the necessary remedial actions if required.

Mercury is a constituent of some ores, and a residual from processing in some tailings. The mercury cyanide complex loads on to carbon and is electrowon. Mercury vapour will become a major health hazard in these circumstances, and special design features are required to capture the mercury.

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Chapter 27

Recent advances in gold refining technology at Rand Refinery

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1. INTRODUCTION

Demands on precious-metals refineries have increased significantly in modern times. Refineries are required not only to compete efficiently in an industry with excess global capacity, but also to be environmentally compliant on a wide range of issues. While in the past, economy of scale dominated, a relatively small refinery with modern technology can now prosper. Therefore, the well-established large refineries need to constantly review their processes and update their technology, automate and computerize where advantageously applicable, and, together with their economy of scale, continue to provide the most cost effective and competitive precious-metal refining service.

Refining processes and technology need to be benchmarked against the following main criteria:

- Process speed
- Process inventory
- Metal-recovery rates
- Recirculating loads
- Cost
- Risk of theft
- Accurate metallurgical accounting for receipts, in process material and final product
- Flexibility to treat a wide range of material
- Ability to meet market quality requirements
- Compliance with environmental, health and safety standards.

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While this chapter focuses on advances in the refining of gold at the Rand Refinery, much of this information applies to the other commercial refineries that collectively produce the majority of the world's gold bullion. Further information pertaining to the refining of gold along with base metals and platinum group metals (PGMs) may be found in Chapters 35 and 36, respectively.

Having successfully used and proven its evaluation process over some 85 years of operation, Rand Refinery remains convinced that the melting of gold and silver *doré* receipts in an induction furnace is imperative in order to obtain a completely representative sample of gold and silver content for analysis. Of special importance to gold refineries is the segregation in *doré* bars of the gold/silver/lead/zinc alloys produced in cyanide mills, shown in Fig. 1. The classic and earliest illustration of this is of an investigation by Matthey (1896), where one *doré* bar of 120 oz assayed 662 ppt gold at the bottom corners, and only 439 ppt at the top. This early experience confirms that only when melting, and with the excellent mixing action of an induction furnace, can a completely accurate sample for analysis be obtained.

Since melting each *doré* receipt, which is mainly in the form of rough bars, is a prime requisite for evaluation, it follows that the classical Miller process (shown in Fig. 2) continues to be rated the best subsequent process for the removal of base metals, primarily due to the speed of the process and its low

Fig. 1. Doré bars arriving from a mine.

Fig. 2. Refining furnace in the Miller refining circuit.

inventory requirement. The process has been continuously optimized by Rand Refinery over many years.

The Miller process can produce marketable 9950 grade gold and meets the majority of the above-mentioned criteria. However, the subsequent process of electrorefining to refine 9950 grade gold to 9999 grade does not meet all the criteria and has therefore been carefully reviewed and investigated over the past 5 years. This led to the decision to purchase a high-speed silver-electrolysis plant (HSSE) that was commissioned in August 2000 and is depicted in Fig. 3. This plant was installed to prove the practicability of the process principle, with the intention, if proved to be satisfactory, of applying it to improving the gold-electrolysis operation.

The electrorefining process (see also Chapter 26) is still considered the process of choice, for several reasons:

- electrolytic dissolution is superior to chemical dissolution for numerous reasons, speed being the most important;

Fig. 3. The HSSE plant.

- simultaneous dissolution and deposition results in not only high speed, but also requires much smaller solution volumes (and hence, a significantly smaller plant size) than wet-chemical refining processes, especially when the process is catering for tonnage quantities of gold; and
- the electrolytic refining process uses very few chemicals or reagents, while effluent arisings are almost negligible, which, in turn, practically ensures 100% gold recovery.

2. EVALUATION

The accurate and precise evaluation of incoming customer *doré* and smelter material forms the first vital step in the refining process.

Doré is delivered to the refinery by helicopter or road and is received into the refinery through a double door airlock arrangement. The *doré* is removed from the packaging and is weighed in its as received form to give a 'wet' weight. The *doré* is then dried in a two-stage drying process that is resistance heated to a temperature of 120 °C to dry off any entrained moisture. Following this, the *doré* is weighed on three separate scales, each accurate to 0.10 g. The mean of these three values is automatically calculated and

Fig. 4. Pouring a gold button prior to analysis by fire assay.

recorded in the database of the metallurgical-accounting system as the official delivered weight of the customer's *doré*.

Following the weighing process, the *doré* is melted in an induction furnace. Four sets of dip samples are taken from the molten metal, as shown in Fig. 4. This allows for quadruple analysis by each of two X-ray spectrophotometry streams and two fire-assay streams, i.e., a total of 16 determinations. The X-ray result is known within 12 min and this value is used to price the customer's deposit on the same day that it was delivered. The fire-assay results are used to effect payment on the second day after delivery. This important step in the process has received a high level of attention of late, to the extent that Rand Refinery's analytical laboratory is capable of achieving a fire-assay precision (as measured by the standard deviation from the mean) of less than 0.01% and a fire assay accuracy (as measured by the divergence from the mean) of less than 0.005%. These exacting standards were achieved as a result of the stringent two-year process of accreditation as a good-delivery referee for the London Bullion Market Association (LBMA), an accolade that Rand Refinery achieved in January 2004, placing it amongst the top five refiners in the world.

Rand Refinery's analytical facility is considered to be state of the art in that it is highly instrumented, utilizing X-ray spectroscopy, spark-emission spectroscopy and inductively-coupled plasma spectroscopy in addition to the traditional fire-refining techniques. This provides the ability to analyse precious metals for virtually every element on the periodic table.

Material being delivered into the smelter plant also benefits from the high levels of expertise and technology in the evaluation department. The smelter treats a wide range of material including borax slag, gravity concentrates, electronic scrap and catalysts. These materials are subjected to the same high levels of sampling accuracy and assay precision as for refinery *doré*. The smelter treats 3800 t of material per year which is all weighed, sampled and assayed in a purpose-designed plant ahead of the arc furnace (as described in Section 5).

3. THE HIGH-SPEED SILVER-ELECTROLYSIS PLANT OPERATION

As the process is patented and Rand Refinery has signed a non-disclosure agreement with Prior Engineering AG, permission has been granted to describe the plant and process in general, while certain details and know-how are withheld.

The process is based on the Moebius and Balbach Thum electrolytic processes. The main change is the use of an anode basket (see Fig. 5) for containing silver granules instead of the conventional cast-silver anodes. The design allows continuous operation by continuously separating anode sludge, or essentially high-grade gold slime, from the bottom of the anode basket. By using granules and a specific operational technique, a 10–15-fold increase of effective anode surface area is achieved compared to conventionally cast silver anodes of similar dimension. This allows cell operation at multiples of the maximum current of the conventional cell, increasing productivity per cell significantly, while, with the lower anode current density, the quality of cathode is improved to at least 9999 quality silver. In addition, the process can accommodate significantly higher levels of anode impurities than the conventional Moebius or Balbach Thum electrolytic cells, of up to 20% gold, copper, base metals or palladium, and still produce 9999 silver quality product. Impurity levels quoted are the individual maxima, as anode silver should exceed 80%.

Compared to Rand Refinery's existing 23-cell Moebius electrolytic plant with a capacity of 120 t of 9990 silver capacity per annum, the HSSE plant has a capacity of 80 t of 9999 silver capacity per annum requiring only four cells, and the plant *footprint* is very much smaller, as shown in Fig. 6.

Fig. 5. Silver granules as used in the anode baskets of the HSSE plant.

The cathode design is essentially conventional with only minor changes. Silver crystals deposited on the cathode are continuously removed with mechanical scrapers, recovered from the bottom of the cell mechanically, automatically two-stage washed, and enter a centrifuge where they are pre-dried.

The electrolyte silver tenor is maintained by making up with solution produced from anode-quality silver in the integrated electrolyte-recycle system (hydrolysis unit), which removes impurities from the electrolyte by precipitation under elevated temperature and pressure. This arrangement results in a zero-effluent operation and NO_x emissions are almost totally eliminated, while base-metal impurities and PGMs are removed as metal oxide solids.

The electrolysis, hydrolysis and dissolution units are all automatically controlled by a single computer, which, together with the continuous operation of the system, reduces labour requirements to a minimum.

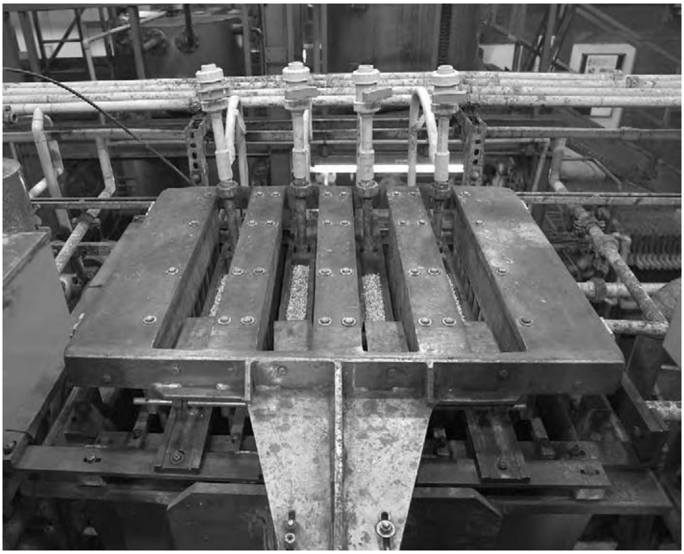

Fig. 6. An electrolytic cell in the HSSE plant.

Due to the high speed and continuous operation of the process, gold inventory when refining silver containing up to 20% gold is minimized. Also, the process is far more suitable for treating silver containing such high quantities of gold than conventional silver electrolytic processes. The Miller process is unsuitable for *doré* with a silver content higher than 50%.

As a rule, all new technology is not without problems and this plant proved not to be the exception. (The first plant was installed at Western Mining Corporation's Olympic dam expansion project, Australia, and commissioned in August 1999. However, it was decided to continue using their old plant. Another plant was installed at Ohio Precious Metals Inc., USA, and has been commissioned and operated since August 2002.)

The initial use of a single transformer servicing all four cells in series resulted in silver being deposited in the silver-crystal conveyor system, causing intermittent breakdowns. However, once the supplier replaced the single transformer with a transformer serving each cell, this problem was resolved. It was learnt that a single transformer could only be used with multiple cells in series at a low-power input.

The second major problem experienced was that, while design power on the cell was initially achieved, over time the power input progressively dropped due to very fine anode slime blocking the outer anode-basket diaphragm. Once the blocked outer diaphragm was replaced, design (rating) power was again achieved but again deteriorated over time.

Fig. 7. 1,000 oz good-delivery silver bars.

This problem was resolved by changing the type of diaphragm that is used. Various improvements and design changes to the anode underflow or extraction system have also assisted in resolving this problem.

Generally, it took longer than anticipated for operating and maintenance personnel to become accustomed to the operation of the new computerized plant, resulting in lower than design plant utilization being achieved. However, the mechanical and control problems have been resolved and close to 100% utilization is now achieved. A large proportion of the equipment, such as pumps and valves, has been replaced with locally manufactured equivalents, resulting in a marked improvement in spares availability, and, consequently, a much improved plant utilization.

The HSSE plant is now achieving design output rate, plant utilization and product quality (Fig. 7).

4. GOLD ELECTROLYSIS

The well-known Wohlwill electrolytic process has served the industry well for over 100 years. Little change or innovation has, however, occurred during this period. Although most of the process criteria are met, conformance with three critical elements, viz., process speed, as well as minimal process inventory and recirculating loads, is less than acceptable and needs to be improved.

Rand Refinery has, since its inception, used the *aqua regia*-based electrolytic operation, shown in Figs. 8–10. To maximize cell production rate in order to minimize electrolyte gold inventory, the practice at Rand Refinery is to operate each electrolytic cell at well over the critical current density normally required to maintain equilibrium operating conditions. Above this critical current density, gold cathode deposition rate exceeds anode dissolution rate and electrolyte gold tenor decreases. The current practice is to make a daily addition of nitric acid to each cell to maintain electrolyte gold tenor or cell equilibrium.

Although the addition of nitric acid increases the anode dissolution rate and maintains electrolyte gold tenor, the production of metallic gold sludge also occurs. Gold sludge make is in the order of 10% of anode weight charged. This has to be manually removed from the cell each day, before washing to remove entrained electrolyte, and then has to be melted, the silver-chloride slag removed, cast into anodes and returned to the electrolytic cell.

Investigations aimed at reducing or eliminating gold sludge make have been unsuccessful. Gold sludge make is attributed to the formation of monovalent gold as aurous chloride (AuCl) rather than the more stable acidic gold chloride ($HAuCl_4$) or trivalent gold chloride, which ionizes as follows:

$$\mathrm{HAuCl_4} \rightarrow \mathrm{AuCl_4^-} + \mathrm{H^+} \tag{1}$$

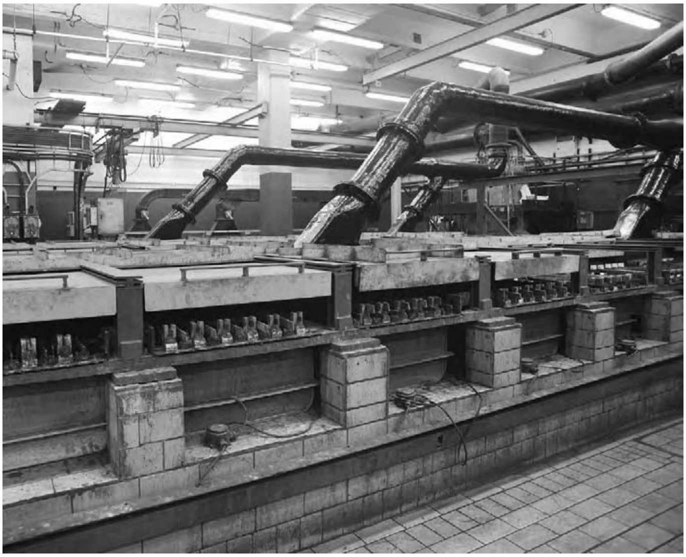

Fig. 8. Electrolytic cells used to produce 9999s purity gold.

Fig. 9. 9999s sponge gold on a cathode plate.

Fig. 10. Electrolytic cells showing the titanium cathode plates.

The electrolytic process is therefore:

At the cathode:

$$AuCl_4^- \rightarrow Au^{3+} + 4Cl^- \tag{2}$$

$$Au^{3+} + 3e \rightarrow Au \tag{3}$$

At the anode:

$$Au \rightarrow Au^{3+} + 3e \tag{4}$$

$$Au^{3+} + 4Cl^- \rightarrow AuCl_4^- \tag{5}$$

Gold sludge is invariably found directly below the anode and in higher purity. The cathode gold current efficiencies based on trivalent cathode gold and monovalent gold sludge makes, also confirm a chemical mechanism for sludge precipitation.

As the electrolyte is *aqua regia*, it would be expected to dissolve the metallic gold sludge arisings. However, this does not typically occur because the electrolyte *aqua regia* concentration is too low. The normal *aqua regia* reaction is as follows:

$$HNO_3 + 3HCl \rightarrow 2H_2O + Cl_2 + NOCl \tag{6}$$

$$NOCl + H_2O \rightarrow HNO_2 + HCl \tag{7}$$

$$3HNO_2 \rightarrow HNO_3 + 2NO + H_2O \tag{8}$$

Thus, the liberated chlorine dissolves gold to form the trivalent auric chloride, while the nitrosyl chloride, having a boiling point of −6 °C to −8 °C, is readily hydrolysed by water to nitrous acid and hydrochloric acid (Eq. (7)). Nitrous acid, being very unstable, decomposes to nitric acid, nitric oxide and water (Eq. (8)). The total dissolution reaction is therefore the evolution of chlorine, with the formation of hydrochloric acid and nitric acid, products useful to the initial reaction (Eq. (6)), with the liberation of nitric oxide.

The electrolyte *aqua regia* concentration and conditions are not favourable for dissolving the metallic gold sludge formed, but with the positive electrode influence or field of the anode it would appear that anode gold will chemically dissolve to restore the electrolyte gold-tenor equilibrium, due to the liberation of chlorine. However, the nitrosyl chloride produced reacts with the trivalent auric chloride in solution to form monovalent gold or aurous chloride:

$$2NOCl + AuCl_3 \rightarrow AuCl + 2Cl_2 + 2NO \tag{9}$$

Aurous chloride is, however, very unstable and readily breaks down to the stable auric chloride and metallic gold, resulting in metallic gold sludge being produced:

$$3AuCl \rightarrow 2Au + AuCl_3 \qquad (10)$$

The foregoing is the most likely explanation of how nitric acid addition to the cell allows critical anode current density to be exceeded, electrolyte gold-tenor equilibrium to be maintained and of how the undesirable metallic gold sludge is formed.

Testwork to reduce or eliminate gold-sludge production in the electrolytic cell has indicated that to maintain electrolyte gold tenor at higher than equilibrium current densities, the addition of gold solution is preferable to nitric acid addition to the cell, while nitrate-free gold solution further improves the operation.

Rand Refinery is currently planning to install gold-dissolution equipment to allow efficient production of auric chloride solution, utilizing the hydrochloride and chlorine-gas process. While the addition of auric chloride solution to the cell will reduce gold sludge make, it will also allow operation at even higher current densities. However, these improvements will not fully optimize the gold-electrolysis operation. To further optimize the process speed, minimize gold inventory and considerably reduce circulating loads, it is planned to pilot the application of high-speed gold electrolysis (HSGE).

Numerous exercises have been completed by Rand Refinery technical staff, independent consultants and another gold refiner to compare the operating cost of the electrolytic process, the classical wet-chemical process, and the more recent wet-chemical/solvent-extraction process (Feather *et al.*, 1997). The studies confirmed that Rand Refinery's current electrolysis was the most cost-effective process, even before conversion of the current electrolytic operation to a chloride-only operation. However, should the HSGE process prove to be successful, the improvements envisaged will make a further significant improvement. While the equipment required to produce nitrate-free gold-chloride solution will be used for improving the current operation, it is also required for the HSGE pilot-plant operation; and if piloting is successful, it will also be used for the HSGE operation.

The three main criteria that conventional electrorefining does not meet are largely achieved by utilizing the Prior HSGE technique:

- *Speed* – electrolytic gold cathode is available 12 h sooner, the electrolytic deposition rate being increased some sixfold.
- *Inventory* – the gold content of electrolyte inventory is reduced by over 80%, owing to the increased productivity per cell or more efficient electrolyte utilization.

- *Circulating load*s – anode stub and anode sludge recirculating loads are eliminated.

Since the application of the Prior HSSE process has now been successfully completed, it is intended to commence the piloting of the process for gold electro-refining. The advantages of the process outlined could possibly be applied to other metallurgical applications, such as the electrorefining of copper. In copper electrorefining, the productivity per cell is conventionally dictated by the maximum current density of the cathode. This is considered a limitation because when the critical current density is exceeded, three factors usually result in the equilibrium of the operation being disturbed. First, the electrolyte tenor drops and the anode is now considered to be passivated. Second, with the longer copper-cathode plating cycles (±14 days), nodule growth on the cathode increases; resulting in, third, lower power efficiencies.

Trials with anode baskets to contain copper granules have also been unsuccessful owing to excessive corrosion of the basket in the powerful electrolytic field environment.

The Prior design of anode basket successfully obviates this corrosion problem. Maintaining electrolyte copper tenor equilibrium by supplementation with copper sulphate solution, together with mechanical removal of cathode nodules, could possibly result in the process being applied to electrolytic copper-refining operations. With the massive scale of copper electrorefining plants, it might be difficult for operators to justify conversion to the high-speed copper-electrolysis process. However, the economics for using the process for extensions or new plants should be distinctly favourable.

5. RAND REFINERY SMELTER OPERATIONS

The Rand Refinery smelter receives a large variety of gold- and silver-bearing material from South African and international gold producers, gold and silver processors and scrap-recovery operations. Gold, silver and PGMs are efficiently and cost-effectively recovered from these materials using pyrometallurgical processes.

In 1966, the existing facilities were modernized by the installation of six basic operations – sampling, blending and sintering, blast-furnace smelting, cupellation, pan-furnace smelting and fume collection. At that time, this was considered to be state-of-the-art technology.

In 1986, the sinter plant, blast furnace and cupellation units were replaced by a 2.2 MVA electric-smelting furnace and a top-blown rotary converter. This was done not only to improve efficiencies and reduce costs, but also to reduce the cost of meeting both environmental and health and safety requirements. In 1992, a new feed-blending plant was installed and the top-blown converter replaced by the more efficient bottom-blown oxygen converter for cupellation, depicted in Fig. 11.

The twin-stream blending and continuous-sampling plant includes a single conical and three ribbon blenders together with continuous cross-belt samplers for sampling customer deposits. Considerable effort over numerous years has been put into developing reliable and accurate primary and sub-sampling methods for the very wide range of materials that are received. It has been found that screening out the metallics from the whole sub-sample is essential to leave a fines bulk sample that is more uniform and can subsequently be accurately split. The total metallics sample, if large, is smelted, fluxed if required and the molten sample sub-sampled or, if small, the total assayed. The metallic and fines assays are combined according to their masses to calculate the overall deposit lot analysis.

Smelter recoveries of gold, silver and PGMs are high due to the twin matte and lead collection phases used. Gold, silver and PGMs report predominantly to the lead phase, while base metals report to the matte phase. Lead and matte are tapped separately (shown in Fig. 12), lead being charged to the bottom-blown oxygen converter for cupellation and matte, solidified, crushed and recirculated back to the electric furnace. *Doré* with +99%

Fig. 11. Preparing to pour *doré* from the bottom-blown oxygen converter.

Fig. 12. Slag tapping from the arc furnace.

gold, silver and PGMs produced by cupellation is sent to the refinery. When base metals in matte reach sufficiently high values, excess matte is bled from the circuit for recovery of both base and precious metals overseas.

To provide a full service to customers, activated-carbon fines receipts are incinerated in a fully autogenous, continuous, fluid-bed incinerator and the ash produced is included in the electric arc-furnace feed. This facility also provides a cost-effective service for small gold-mine operations without activated-carbon elution facilities for the recovery of gold and silver.

6. SMALL-BAR PLANT

A new fully automated production facility was commissioned in 1998 to produce small bars, mostly in the 100–1,000 g range. The facility automatically weighs out gold granules to the exact bar weight. The weighed granules are induction melted to produce a full range of high-quality gold bars (Fig. 13). Bars are packed and shipped directly to customers via Rand Refinery's vault facility at Johannesburg International Airport. This vault serves the total South African gold and platinum industry, by handling receipts from international customers, and despatching refined precious-metal products worldwide.

Fig. 13. Kilobars after check weighing.

7. CERTIFICATION AND ACCREDITATION

Rand Refinery is certified compliant with the requirements of ISO 9001 (quality) and ISO 14001 (environmental) and has recently been awarded certification under OHSAS 18001 (Heath and Safety). Furthermore, the refinery has held good delivery accreditation to the LBMA since 1921, and has recently been accredited as a good-delivery referee, as mentioned earlier. The high standard of engineering maintenance at the company was rewarded in 2003 when Rand Refinery was declared a gold medallist by the South African Maintenance Association, in addition to being the national champion company for maintenance excellence.

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Peter H. Radcliffe was born in England and graduated in metallurgy at Cambridge University. His career has been almost entirely with Anglo American and Anglogold Ashanti in various operating, technical and managerial capacities. He relinquished his position Head of Metallurgy with Anglogold Ashanti to become Managing Director of Rand Refinery and has recently retired.

Phil J. Mostert graduated in chemistry from the University of Cape Town and during his subsequent career with Anglo American served on the Zambian copper belt and later as consulting metallurgist for Zimbabwe. Shortly after his return to South Africa he was appointed general manager of Ergo, and then completed his career as managing director of Rand Refinery from 1994 to 1999, where he currently consults.

II.6 *Disposal of Residues and Effluents*

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Chapter 28

Cyanide treatment: Physical, chemical and biological processes

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Several proven and effective chemical, physical and biological treatment processes have been developed for the removal and recovery of cyanide from mill tailings and process solutions. These treatment processes are well understood and have been utilized for many years at mine sites worldwide. The purpose of this chapter is to provide background information regarding these cyanide treatment processes, including basic chemistry and reagent usages, common areas of application and treatment performance that can be expected at full-scale. Emphasis is placed upon those treatment processes with proven full-scale success, as well as those processes exhibiting significant potential for specific application at mine sites.

1. INTRODUCTION

In the mining industry, cyanide is primarily used for leaching gold and silver from ores, but it is also used in low concentrations as a flotation reagent for the recovery of base metals such as copper, lead and zinc. At many of these operations, cyanide treatment systems may be required to

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address potential toxicity issues in regard to the health of humans, wildlife, waterfowl or aquatic life. This may include the removal of cyanide from one or more of the following:

- Slurry tailings from cyanidation operations
- Excess solution from Merrill–Crowe operations
- Excess solution from heap or tank leaching operations
- Supernatant solution from tailings storage facilities
- Seepage collected from ponds or tailings storage facilities.

Cyanide treatment is generally classified as either a destruction- or a recovery-based process. In a cyanide-destruction process, either chemical or biological reactions are utilized to convert cyanide into another less toxic compound, usually cyanate. Cyanide recovery processes, described in more detail in Chapter 29, are a recycling approach in which cyanide is removed from the solution or slurry and then re-used in a metallurgical circuit.

Selection of an appropriate cyanide-treatment process for a particular site involves the consideration of many factors, but normally the number of candidate processes for a particular application can be narrowed following review of the untreated solution or slurry chemistry, the desired effluent quality and the availability of reagents or suitable process waters. Common applications for cyanide treatment in the mining industry are described below:

- *Tailings slurry treatment* is employed when the cyanide level must be lowered prior to being discharged into a tailings storage facility. In this application, the initial tailings slurry weak acid dissociable (WAD) cyanide level typically ranges from about 100 to 500 mg/L and treatment to less than 50 mg/L cyanide is commonly established as the goal for wildlife and waterfowl protection (Hagelstein and Mudder, 2001; ICMI, 2002).
- *Solution treatment* is employed when the cyanide level in decant or process solution must be lowered prior to being discharged into the environment. Treatment of WAD cyanide to low levels is normally required to ensure the protection of human health or aquatic ecosystems. Treatment technologies for solutions commonly employ chemical oxidation and polishing processes, which are applicable to relatively low concentrations of cyanide and generate high-quality effluent.

2. CYANIDE MANAGEMENT PLAN

A key component in relation to treating cyanide is development of a site-wide cyanide-management plan. The importance of properly developing and administering such a plan has been highlighted by incidents at mine sites involving the inadvertent release of cyanide to the environment (Mudder and Botz, 2001a). Aside from the potential for environmental impact, such incidents broadly and negatively affect the image of the mining industry and have led to emotional and damaging political responses, such as the banning of cyanide in some regions.

Numerous guidance documents have been developed with regard to cyanide management, and these documents should serve as a template for developing site-specific cyanide management plans at mine sites (CMSA, 2001; ICMI, 2002; ECIC, 2003; Cyantists, 2004; Mudder and Botz, 2004). Implementation and adherence to a cyanide-management plan, augmented by experienced scientific and engineering judgement, will help reduce both the number and severity of environmental incidents involving cyanide. The International Cyanide Code (ICMI, 2002) is one such plan that is attracting significant commitment from the international gold mining community and is reviewed in Chapter 8.

The management of water and cyanide are intimately related, and development of a cyanide-management plan should proceed in concert with development of a water-management plan. A good cyanide-management plan will include descriptions of how cyanide-containing solutions and slurries will be handled, stored, contained and monitored, and in many cases the plan will also include a description of treatment plants used to remove cyanide from solutions or slurries. At sites where natural cyanide attenuation is important, the cyanide-management plan should address the specifics of predicting and monitoring the effectiveness of the attenuation processes. Decommissioning and closure are important phases in the life cycle of cyanide management and should be addressed in the cyanide-management plan (refer to the chapters in Section I.4).

3. ANALYSIS OF CYANIDE

The term *cyanide* generally refers to one of three classifications of cyanide, and it is critical to define the class of cyanide that is to be treated. The three classes of cyanide are: (1) *total* cyanide; (2) *WAD* cyanide; and (3) *free* cyanide, as shown in Fig. 1. Each of these forms of cyanide has specific analytical methodologies for its measurement, and it is important that the relationship between these forms be understood when analyzing cyanide-containing solutions. As indicated in Fig. 1, for a given solution the total cyanide level is always greater than or equal to the WAD cyanide level, and likewise, the WAD cyanide level is always greater than or equal to the free cyanide concentration.

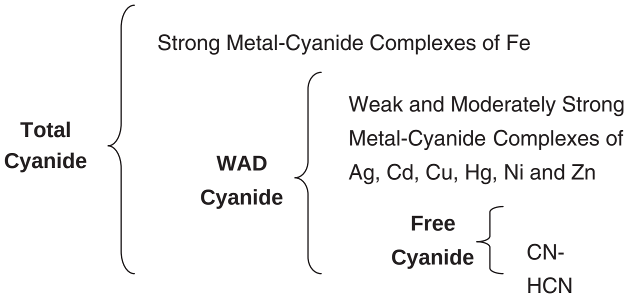

Fig. 1. General classifications of cyanide compounds.

Table 1
Free cyanide and metal-cyanide complexes

Free cyanide	Copper cyanides	Iron cyanides	Nickel cyanides	Zinc cyanides
HCN	$Cu(CN)_2^-$	$Fe(CN)_6^{3-}$	$NiCN^+$	$ZnCN^+$
CN^-	$Cu(CN)_3^{2-}$	$Fe(CN)_6^{4-}$	$Ni(CN)_4^{2-}$	$Zn(CN)_2^0$
	$Cu(CN)_4^{3-}$		$Ni(CN)_5^{3-}$	$Zn(CN)_3^-$
				$Zn(CN)_4^{2-}$
				$Zn(CN)_5^{3-}$

The appropriate approach to assessing the quality of water samples in most situations is to analyse for WAD cyanide since this includes the toxicologically or environmentally important forms of cyanide, including free cyanide and moderately and weakly complexed metal cyanides. Total cyanide includes free cyanide, WAD cyanide plus the relatively non-toxic iron–cyanide complexes. Complete characterization of a cyanide solution generally includes analyses for pH, total cyanide, WAD cyanide, thiocyanate, cyanate, ammonia, nitrate, nitrite and base metals such as copper, iron, nickel and zinc. Total dissolved solids (TDS) and oxidation–reduction potential (ORP) measurements may also be useful. Shown in Table 1 are the free cyanide and metal-cyanide complexes often encountered in cyanidation solutions. Other metals, such as cadmium and mercury, also form complexes with cyanide, but these are normally present at low levels.

4. BIOLOGICAL CYANIDE DESTRUCTION PROCESSES

A wide variety of microorganisms are naturally present in water, including domestic and industrial wastewaters. Biological treatment processes promote the growth and development of large populations of bacteria, which are essential for treatment. Bacteria convert soluble organic contaminants into energy, cell mass and other less toxic by-products. Many microbial species (bacteria, fungi and algae) and plants can detoxify cyanide to environmentally acceptable levels and into less harmful by-products (Akcil, 2003; Akcil and Mudder, 2003; Akcil *et al.*, 2003; Trapp *et al.*, 2003; Gurbuz *et al.*, 2004).

Over the past decade, biological cyanide treatment processes have become increasingly widespread in the mining industry due to their ability to simultaneously remove multiple contaminants, their relatively low operating cost and ability to produce high-quality effluent. Biological treatment processes are used to treat decant solution, or in some cases process solutions, but are normally not suitable as a direct tailings-treatment process.

There are several possible configurations of biological treatment processes, with the general divisions being aerobic vs. anaerobic and attached growth vs. suspended growth. Shown in Table 2 are constituents normally removed in aerobic and anaerobic biological treatment processes. In the *aerobic* process, cyanide, thiocyanate, nitrite and ammonia are oxidized to nitrate, while in the *anaerobic* (or *anoxic*) process, nitrate and nitrite are removed as nitrogen gas. With both processes, incidental metals removal may occur through biomass sorption or precipitation as metal carbonates, hydroxides or sulfides.

With *attached-growth* biological processes, biogrowth occurs on a fixed solid media, for example, in a *rotating biological contactor* (RBC) or *trickling filter*. Periodically, biomass slough from the media are carried away with the effluent. Attached growth systems are generally used with low influent constituent levels to avoid overloading the media with biomass.

With *suspended-growth* biological processes, biogrowth occurs in a suspended sludge system, similar to a slurry suspension. Waste biomass is removed as underflow from a clarifier, with most biomass recycled from clarifier underflow to the feed water stream. Suspended growth systems are generally used with higher influent constituent levels due to the higher rate of biomass growth.

Table 2
Constituent removals in aerobic and anaerobic biological processes

Aerobic biological treatment	Anaerobic biological treatment
Cyanide	Nitrate
Ammonia	Nitrite
Thiocyanate	Metals
Nitrite	
Metals	

The biologically mediated cyanide oxidation reaction is

$$CN^- + \tfrac{1}{2}O_2 + 3H_2O \rightarrow HCO_3^- + NH_4^+ + OH^- \tag{1}$$

The stable iron-cyanide compounds are not biologically oxidized in this process, although a small portion may be sorbed into the biomass. In the above reaction, cyanide is oxidized to ammonia, with about 0.54 g of ammonia (as N) being formed per gram of cyanide oxidized. The oxygen demand for this reaction is about 0.62 g/g of cyanide oxidized, while biomass production is about 0.05–0.10 g/g of cyanide oxidized.

The biologically mediated thiocyanate oxidation reaction is

$$SCN^- + 3H_2O + 2O_2 \rightarrow HCO_3^- + NH_4^+ + SO_4^{2-} + H^+ \tag{2}$$

In this reaction, thiocyanate is oxidized to ammonia and sulfate, with about 0.24 g of ammonia (as N) being formed per gram of thiocyanate oxidized. The oxygen demand for this reaction is about 1.10 g/g of thiocyanate oxidized, while biomass production is about 0.08 g/g of thiocyanate oxidized.

Ammonia generated by cyanide and thiocyanate oxidation is oxidized in the aerobic biological process. The end product of this nitrification reaction is nitrate according to the following reaction:

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O \tag{3}$$

In this reaction, 1 g of nitrate (as N) is formed for each gram of ammonia (as N) oxidized. The oxygen demand for this reaction is about 4.57 g/g of ammonia oxidized (as N), while biomass production is about 0.17 g/g of ammonia oxidized.

Nitrite is also aerobically oxidized according to the following reaction:

$$NO_2^- + \tfrac{1}{2}O_2 \rightarrow NO_3^- \tag{4}$$

The oxygen demand for this reaction is about 1.14 g/g of nitrite (as N) oxidized, with minimal biomass production.

The biological oxidation of cyanide, thiocyanate, ammonia and nitrite occurs simultaneously in aerobic systems, with the thiocyanate reaction being somewhat more rapid and less sensitive to temperature. Often it is necessary to heat water to maintain a treatment temperature of approximately 10–15°C, since lower water temperatures result in slower reaction kinetics and proportionally larger treatment equipment.

Following aerobic treatment, anaerobic (or anoxic) denitrification is often used to remove nitrate and residual nitrite as nitrogen gas:

$$6NO_3^- + 5CH_3OH \rightarrow 3N_2 + 5HCO_3^- + 7H_2O + OH^- \tag{5}$$

Nitrate is converted into inert nitrogen gas in this process (nitrogen gas is the main component of atmospheric air). Total sludge production in this reaction is about 0.55 g/g of nitrate removed. Methanol (CH_3OH) is commonly used as an organic carbon source in this process, although other sources of organic carbon can be used, such as ethanol or molasses.

Active and passive biological cyanide-treatment processes have become relatively widespread in the mining industry due to the success of the first plant installed at the Homestake Lead mine in the USA in the 1980s (Mudder *et al*., 2001a). In this plant, an aerobic attached-growth biological treatment is used to remove cyanide, thiocyanate, cyanate, ammonia and metals from tailings-impoundment decant solution prior to discharge to surface water. The plant has been operating successfully for over 15 years, producing high-quality effluent as summarized in Table 3 (Mudder *et al*., 2001).

A two-stage suspended-growth biological-treatment plant was installed by Homestake Nickel Plate, Canada in the mid-1990s to treat tailings-impoundment seepage. This plant is a suspended-sludge system with both aerobic and anaerobic treatment sections to remove cyanide, thiocyanate, cyanate, ammonia, nitrate and metals. Representative treatment results for this plant are shown in Table 4 (Given *et al*., 2001).

A passive biological-treatment process was installed at the Homestake Santa Fe (USA) mine to treat draindown from a decommissioned heap-leach pad. This process, known as the passive biopass process, is suitable for solution flows of less than about 10 m^3/h for the removal of cyanide, thiocyanate, cyanate, ammonia, nitrate and metals. Representative treatment results for this plant are shown in Table 5.

The applicability of biological processes for the treatment of waters in the mining industry has been somewhat limited until recently. The process applicability is primarily with continuous water flows with temperatures

Table 3
Homestake Lead biological treatment performance

Constituent	Decant solution	
	Untreated (mg/L)	Treated (mg/L)
Total cyanide	3.39	0.37
WAD cyanide	2.34	0.03
Thiocyanate	—	—
Ammonia	5.31	0.27
Nitrate	—	21.9
Copper	0.49	0.04
Iron	0.1–5.0	0.27
Nickel	0.01–0.04	0.03
Zinc	0.01–0.1	0.01

Table 4
Homestake Nickel Plate biological treatment performance

Constituent	Seepage water	
	Untreated (mg/L)	Treated (mg/L)
Total cyanide	1.04	0.44
WAD cyanide	0.33	0.04
Thiocyanate	379	0.08
Ammonia	25.3	0.15
Nitrate	2.8	0.13
Copper	0.02	0.005
Iron	0.06	0.02
Nickel	—	—
Zinc	—	—

Table 5
Homestake Santa Fe biological treatment performance (after Mudder *et al.*, 2001b)

Constituent	Heap-leach pad draindown	
	Untreated (mg/L)	Treated (mg/L)
Total cyanide	—	—
WAD cyanide	14	<0.2
Thiocyanate	—	—
Ammonia	—	—
Nitrate	55.6	0.8
Copper	10.3	<0.5
Iron	—	—
Nickel	—	—
Zinc	—	—

above about 10°C unless water heating is possible. The key advantage to biological treatment is the ability to simultaneously remove several compounds in a single process, often at a much lower cost than would be encountered with other treatment processes. In addition, high-quality effluent can be produced with biological treatment processes, often of a quality suitable for direct discharge to surface water. In situations where cyanide and one or more of its related compounds of cyanate, thiocyanate, ammonia, nitrate and nitrite must be removed, biological treatment should be considered along with conventional chemical treatment processes.

5. CHEMICAL TREATMENT PROCESSES

Most chemical cyanide-treatment processes operate on the principle of converting cyanide into a less toxic compound through an oxidation reaction. Several destruction processes are well proven to produce treated solutions or slurries with low levels of cyanide as well as many metals. In the following sections, several cyanide-destruction processes are discussed along with their typical areas of application. With all of these processes, laboratory or pilot treatability testing is required to confirm the level of treatment achievable and to evaluate the associated reagent consumptions.

5.1. Alkaline chlorination process

Alkaline chlorination, or breakpoint chlorination, at one time was the most widely applied of the cyanide-treatment processes, but it has gradually been replaced by other processes and is now used only occasionally. Alkaline chlorination is effective at treating cyanide to low levels, but the process can be relatively expensive to operate due to high reagent usages. The cyanide-destruction reaction is two-step, the first step in which cyanide is converted to cyanogen chloride (CNCl) and the second step in which cyanogen chloride hydrolyses to yield cyanate:

$$Cl_2 + CN^- \rightarrow CNCl + Cl^- \tag{6}$$

$$CNCl + H_2O \rightarrow OCN^- + Cl^- + 2H^+ \tag{7}$$

In the presence of a slight excess of chlorine at alkaline pH, cyanate is further hydrolysed to yield ammonia in a catalytic reaction:

$$OCN^- + 3H_2O \rightarrow NH_4^+ + HCO_3^- + OH^- \tag{8}$$

If sufficient excess chlorine is available, the reaction continues through *breakpoint chlorination*, in which ammonia is oxidized to nitrogen gas (N_2). The complete removal of ammonia from solutions is a primary advantage of the alkaline chlorination process:

$$3Cl_2 + 2NH_4^+ \rightarrow N_2 + 6Cl^- + 8H^+ \tag{9}$$

In addition to reacting with cyanide, cyanate and ammonia, the alkaline-chlorination process will preferentially oxidize thiocyanate, which in some cases can lead to excessively high consumptions of chlorine. It is the removal of ammonia and thiocyanate that makes this cyanide-treatment process unique when compared to other chemical-oxidation processes:

$$4Cl_2 + SCN^- + 5H_2O \rightarrow SO_4^{2-} + OCN^- + 8Cl^- + 10H^+ \tag{10}$$

The primary application of the alkaline-chlorination process is with solutions rather than slurries due to the high consumption of chlorine that occurs in slurry applications. The process is typically applied to treat low solutions flows initially containing low to high levels of cyanide, to achieve cyanide levels that may be suitable for discharge. The process is effective for the treatment of solutions for the oxidation of free and WAD cyanides, but a lesser amount of iron cyanides are removed depending on the levels of other base metals in the solution being treated. As can be seen in the treatment reactions, a significant increase in the treated water dissolved-solids concentration may result, particularly with chloride.

The theoretical usage of Cl_2 to oxidize cyanide to cyanate is 2.73 g Cl_2/g of CN^- oxidized, but in practice the actual usage ranges from about 3.0 to 8.0 g Cl_2/g of CN^- oxidized. The Cl_2 used in the process can be provided as compressed liquid Cl_2, as a 12.5% solution of sodium hypochlorite (NaOCl) or as a solution of calcium hypochlorite ($Ca(OCl)_2$) prepared from solid calcium hypochlorite. In addition, the above reactions generate varying amounts of acid, which is typically neutralized by adding lime or sodium hydroxide to the reaction vessels.

The reaction is carried out at a pH of greater than about 10.5 to ensure that the potentially irritating cyanogen chloride is rapidly hydrolysed to cyanate. At neutral or acidic pH values, cyanogen chloride may evolve as a relatively toxic gas. An advantage of the process is that copper is not required as a catalyst, as with the SO_2/air process and the hydrogen peroxide process. Upon completion of the cyanide-oxidation reaction, metals previously complexed with cyanide, such as copper, nickel and zinc, are precipitated as metal-hydroxide compounds.

Representative results for treatment of solution via alkaline chlorination are shown in Table 6.

Table 6
Treatment results using the alkaline chlorination process (after Ingles and Scott, 1987)

Constituent	Solution	
	Untreated (mg/L)	Treated (mg/L)
Total cyanide	2,000	8.3
WAD cyanide	1,900	0.7
Copper	290	5.0
Iron	2.4	2.8
Zinc	740	3.9

5.2. Sulfur dioxide and air process

The sulfur dioxide (SO_2) and air process was developed by INCO Limited in the 1980s and is currently in operation at over 30 mine sites worldwide. The process utilizes SO_2 and air at an alkaline pH in the presence of a soluble copper catalyst to oxidize cyanide to the less toxic compound cyanate (OCN^-):

$$SO_2 + O_2 + H_2O + CN^- \xrightarrow{Cu^{2+}\text{ catalyst}} OCN^- + SO_4^{2-} + 2H^+ \tag{11}$$

The theoretical usage of SO_2 in the process is 2.46 g of SO_2/g of CN^- oxidized, but in practice the actual usage ranges from about 3.5 to 5.0 g SO_2/g of CN^- oxidized. The SO_2 required in the reaction can be supplied either as compressed liquid sulfur dioxide or a reduced-sulfur salt such as sodium *meta*bisulfite ($Na_2S_2O_5$), sodium sulfite (Na_2SO_3) or ammonium *bi*sulfite (NH_4HSO_3).

Oxygen (O_2) is also required in the reaction and is normally supplied by sparging atmospheric air into the agitated reaction vessel. The reaction is typically carried out at a pH of about 8.0–10.0 in one or more agitated tanks and lime is added to neutralize the acid formed in the reaction. Lime usage is generally of the order of about 3.0–5.0 g/g of CN^- oxidized. As indicated, copper (Cu^{2+}) is required as a catalyst, and is usually added as a solution of copper sulfate ($CuSO_4 \cdot 5H_2O$) to provide a copper concentration in the range

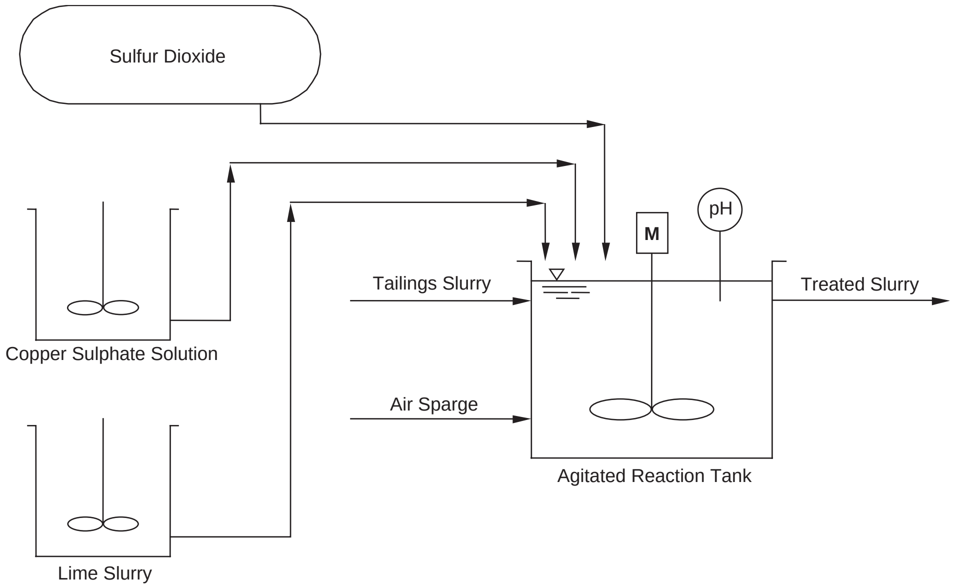

Fig. 2. Sulfur dioxide and air cyanide destruction process.

of about 10–50 mg/L, depending upon the influent cyanide level. In solutions where sufficient copper is already present, supplemental addition of copper may not be required. A general flowsheet for the SO_2/air process is shown in Fig. 2.

Upon completion of the cyanide-oxidation reaction, metals previously complexed with cyanide, such as copper, nickel and zinc, are precipitated as metal-hydroxide compounds. Iron cyanide removal is effected through precipitation as a copper–iron-cyanide complex. The process does not remove thiocyanate to low levels, although a few percent of this cyanide-related compound are typically removed during treatment.

The primary application of the sulfur dioxide and air process is with slurry tailings, but it is also effective for the treatment of solutions for the oxidation of free and WAD cyanides. Representative results for treatment of solution and slurry with the sulfur dioxide and air process are shown in Table 7 (Ingles and Scott, 1987).

5.3. Copper-catalysed hydrogen peroxide process

The copper catalysed hydrogen peroxide treatment process chemistry is similar to that described for the sulfur dioxide and air process, but hydrogen peroxide is utilized rather than sulfur dioxide and air. With this process, soluble copper is also required as a catalyst and the end product of the reaction is cyanate:

$$H_2O_2 + CN^- \xrightarrow{Cu^{2+}\text{ catalyst}} OCN^- + H_2O \tag{12}$$

The primary application of the hydrogen peroxide process is with solutions rather than slurries due to the high consumption of hydrogen peroxide that occurs in slurry applications. The process is typically applied to treat moderate to low levels of cyanide to achieve effluent quality that may be suitable for discharge. The hydrogen peroxide process is effective for the treatment of solutions for the oxidation of free and WAD cyanides, and iron cyanides are removed through precipitation of insoluble copper–iron-cyanide complexes. As indicated in Eq. (12), hydrogen peroxide reacts with cyanide to form

Table 7
Treatment results using the sulfur dioxide and air process

Constituent	Solution		Tailings slurry	
	Untreated (mg/L)	Treated (mg/L)	Untreated (mg/L)	Treated (mg/L)
Total cyanide	450	0.1–2.0	115	0.1–1.0
Copper	35	1–10	17	0.2–2.0
Iron	1.5	<0.5	0.7	0.02–0.3
Zinc	66	0.5–2.0	18	<0.01

cyanate and water, a process that limits the build-up of dissolved solids in the solution being treated.

The theoretical usage of H_2O_2 in the process is 1.31 g H_2O_2/g of CN^- oxidized, but in practice the actual usage ranges from about 2.0 to 8.0 g H_2O_2/g of CN^- oxidized. The H_2O_2 used in the process is typically provided as a concentrated liquid at 50% or 70% strength.

Although the reaction can be carried out over a wide pH range, it is usually conducted at a pH of about 9.0–9.5 for optimal removal of residual metals such as copper, nickel and zinc initially complexed to cyanide. If iron cyanide must also be removed to low levels, then a lower pH is needed to maximize the precipitation of copper–iron-cyanides at the expense of lowering the removal efficiencies of copper, nickel and zinc.

As indicated, copper (Cu^{2+}) is required as a soluble catalyst, which is usually added as a solution of copper sulfate ($CuSO_4 \cdot 5H_2O$) to provide a copper concentration in the range of about 10–50 mg/L, depending upon the initial cyanide and copper levels. Upon completion of the oxidation reaction, metals previously complexed with cyanide, such as copper, nickel and zinc, are precipitated as metal-hydroxide compounds.

Representative results for treatment of solution with the hydrogen peroxide process are shown in Table 8.

With slurry treatment, excess dosages of hydrogen peroxide are required due to the catalytic breakdown of hydrogen peroxide that occurs in the presence of small mineral solids. As with the sulfur dioxide and air process, this process does not remove thiocyanate to low levels, but does remove a few percent of this cyanide-related compound during treatment.

5.4. Caro's acid process

Peroxy*mono*sulfuric acid (H_2SO_5), also known as Caro's acid, is a reagent used in a cyanide treatment process that has found application at a few sites. Caro's acid is produced by reacting concentrated hydrogen peroxide and sulfuric acid in a controlled temperature environment (Norcross, 1996). Production of Caro's acid is typically conducted with 1.5–3.0 mol H_2SO_4/mol

Table 8
Treatment results using the hydrogen peroxide process (after Mudder *et al.*, 2001)

Constituent	Solution	
	Untreated (mg/L)	Treated (mg/L)
Total cyanide	19	0.7
WAD cyanide	19	0.7
Copper	20	0.4
Iron	<0.1	<0.1

H_2O_2 for an overall product yield of up to 80% (based on H_2O_2). Normally, 70% hydrogen peroxide solution and 98% sulfuric acid solution are used to generate Caro's acid:

$$H_2O_2 + H_2SO_4 \rightarrow H_2SO_5 + H_2O \tag{13}$$

Due to its instability, Caro's acid is produced on-site and used immediately for cyanide detoxification with only minimal intermediate storage. At room temperature, Caro's acid is stable for several hours; however, at elevated temperature it is stable only for several minutes, decomposing to liberate oxygen, water and sulfur trioxide (SO_3). Due to its instability, treatability testing of the Caro's acid process is typically conducted using a solid form of the reagent such as potassium peroxy*mono*sulfate (also referred to as *Caroat* or *Oxone*).

The oxidation reaction of Caro's acid with cyanide is

$$H_2SO_5 + CN^- \rightarrow OCN^- + SO_4^{2-} + 2H^+ \tag{14}$$

The theoretical usage of H_2SO_5 in the process is 4.39 g H_2SO_5/g of cyanide oxidized, but in practice 5.0–15.0 g H_2SO_5/g of cyanide oxidized is required. Acid produced in the reaction is typically neutralized with lime, if necessary, and the reaction is normally carried out at a pH in the range of about 7.0–10.0. Note that the oxidation reaction proceeds without the need for a soluble copper catalyst, as is the case for the sulfur dioxide and air process and the hydrogen peroxide process.

Caro's acid is normally used in slurry treatment applications where the addition of a copper catalyst is not desirable. In solution applications, other destruction processes, such as the hydrogen peroxide process, are often preferred. A flowsheet for the Caro's acid process is shown in Fig. 3.

Representative results for treatment of slurry with Caro's acid are shown in Table 9.

Generally, the best application of this process is with tailings slurries containing low to moderate initial levels of cyanide and when treated, cyanide levels of less than about 10–50 mg/L are required.

5.5. Iron-cyanide precipitation

Free, WAD and total cyanides will all react with ferrous iron to yield a variety of soluble and insoluble compounds, primarily hexacyanoferrate(III) ($Fe(CN)_6^{3-}$), Prussian blue ($Fe_4[Fe(CN)_6]_3$) and other insoluble metal-iron-cyanide ($M_xFe_y(CN)_6$) compounds such as those of copper or zinc (Adams, 1992):

$$Fe^{2+} + 6CN^- + \tfrac{1}{4}O_2 + H^+ \rightarrow Fe(CN)_6^{3-} + \tfrac{1}{2}H_2O \tag{15}$$

$$4Fe^{2+} + 3Fe(CN)_6^{3-} + \tfrac{1}{4}O_2 + H^+ \rightarrow Fe_4[Fe(CN)_6]_3 + \tfrac{1}{2}H_2O \tag{16}$$

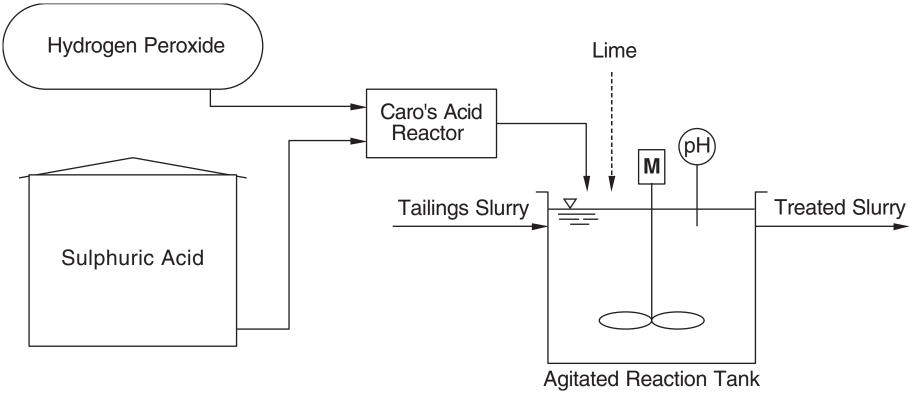

Fig. 3. The Caro's acid cyanide destruction process.

Table 9
Treatment results using Caro's acid (after Castrantas *et al.*, 1993, 1995a, b)

Test number	Slurry WAD cyanide concentration	
	Untreated (mg/L)	Treated (mg/L)
1	44.5	8.5
2	37.5	4.2
3	46.0	14.0
4	39.8	4.0
5	115.0	27.1
6	113.1	16.3
7	101.5	18.7

These reactions act to lower the free and WAD cyanide concentrations by converting them to stable iron-cyanide compounds (soluble and insoluble), while the iron-cyanide concentration is lowered as a result of precipitation reactions.

The iron-cyanide precipitation process is limited to situations where the precipitation reactions can be controlled, and the precipitated solids can be separated from the solution and properly disposed. Proper handling and disposal of the cyanide precipitates generated in the process is important and represents the major disadvantage of this non-oxidative process. In the past, this process was widely used to convert free and WAD cyanides to less toxic iron-cyanide compounds in slurry tailings, but its present utility is primarily as a polishing process to reduce total cyanide concentrations to less than about 1–5 mg/L. There are a number of environmental drawbacks to this process, including the generation of cyanide waste solids and the formation of stable and soluble iron-cyanide compounds that may persist for many years or require further treatment.

The process is optimally carried out at a pH of about 5.0–6.0 or less, and iron is normally added as ferrous sulfate ($FeSO_4 \cdot 7H_2O$). Ferrous sulfate usage ranges from about 0.5 to 5.0 mol Fe/mol CN^- depending on the desired level of treatment (Adams, 1992; Dzombak *et al.*, 1996). As indicated in Table 10, the iron-cyanide precipitation process is capable of achieving relatively low levels of total cyanide at pH 7.0 and an Fe/CN molar ratio of about 4:1 (Dzombak *et al.*, 1996).

5.6. Activated carbon polishing

Activated carbon has an affinity for many metal-cyanide compounds, including the soluble cyanide compounds of copper, iron, nickel and zinc. Activated carbon is suitable for use as a polishing process to remove cyanide to low levels when the initial cyanide concentration is already below about 1–5 mg/L. This is a simple and effective process, convenient for installation at sites where activated carbon is used in metallurgical processes for precious metals recovery. At these sites, newly purchased carbon can be used for water treatment, and then when the carbon breaks through and is no longer suitable for water treatment, it can be transferred to the metallurgical circuit for continued use or thermal regeneration. This has been done at a number of

Table 10
Treatment results using the iron-cyanide precipitation process

Constituent	Solution	
	Untreated (mg/L)	Treated (mg/L)
Total cyanide	8.8	0.89

Table 11
Treatment results using the activated carbon adsorption process (Botz and Mudder, 1997)

Constituent	Solution	
	Untreated (mg/L)	Treated (mg/L)
Total cyanide	0.98	0.20
Copper	0.02	<0.02
Iron	0.22	0.02
Nickel	0.15	0.15
Zinc	0.02	<0.02

sites to produce high-quality effluents without impacting gold recovery operations. At inactive sites, on-site regeneration or off-site disposal of exhausted carbon must be considered.

Representative results for treatment of solution using activated carbon adsorption are shown in Table 11.

5.7. Other cyanide-treatment processes

There are a number of other treatment processes that have been applied at full scale to treat cyanide, but implementation of these processes has been limited for a number of reasons. Ion exchange and reverse osmosis are frequently considered for treatment of solutions, but with both of these processes, waste brine is generated as a by-product. Disposal or further treatment of this brine is difficult and expensive, and in some cases the brine may be hazardous and require special handling. The amount of waste brine generated by ion exchange and reverse osmosis typically ranges from about 5 to 30% of the volume of water treated. Ion exchange and reverse-osmosis processes are also relatively expensive and complex to construct, operate and maintain. Owing to these drawbacks, ion exchange and reverse osmosis are limited to situations where waste brine can be easily disposed or treated, or where very high-quality effluent is required. An advantage of these processes, particularly reverse osmosis, is that in some cases simultaneous removal of cyanide, cyanate, thiocyanate, ammonia, and nitrate can be affected. Ion exchange is occasionally used to target removal of ammonia or nitrate from decant solution.

Ozone is a strong oxidant and capable of oxidizing free and WAD cyanides to cyanate, ammonia and nitrate (Carillo-Pedroza and Soria-Aguilar, 2001; Nava *et al.*, 2003). The reaction rate is rapid and generally only limited by the rate at which ozone can be absorbed into the solution. Low-effluent cyanide concentrations can be achieved with ozone, but treatment may result in the formation of cyanate, ammonia and nitrate. Ozone is relatively expensive to produce and this has limited its use for cyanide destruction, particularly for large water flows, but may find application in small-volume polishing applications. Iron cyanides are also oxidized by ozone, but the reaction rate is too slow at ambient temperature for practical application. At elevated temperature and in the presence of ultraviolet radiation, iron cyanides are converted into cyanate by ozone. Ammonia can be oxidized to nitrate by ozone, but an alkaline pH is required. Thiocyanate is readily oxidized by ozone in a two-step process. In the first step, thiocyanate is oxidized to sulfate and hydrogen cyanide gas:

$$SCN^- + O_3 + OH^- \rightarrow HCN + SO_4^{2-} \tag{17}$$

If the pH of solution is maintained in the acidic range ($pH < 5$), the hydrogen-cyanide gas is inert to further oxidation and can potentially be recycled, neutralized and re-used in leaching (Soto *et al.*, 1996). The cost of the ozone will exceed the value of the cyanide recovered in most cases, so this process is unlikely to find industrial application unless thiocyanate has to be destroyed to meet limits for discharge to the environment, or to maintain sustainable metallurgical performance. Under alkaline conditions, the oxidation reaction continues and the cyanide is further oxidized to cyanate:

$$CN^- + O_3 \rightarrow OCN^- + O_2 \qquad (18)$$

6. NATURAL CYANIDE ATTENUATION

It is well known that cyanide solutions placed in ponds or tailings impoundments undergo natural attenuation reactions, which result in the lowering of the cyanide concentration. These attenuation reactions are dominated by natural volatilization of hydrogen cyanide, but other reactions such as biological degradation, oxidation, hydrolysis, photolysis and precipitation also occur. Natural cyanide attenuation occurs with all cyanide solutions exposed to the atmosphere, whether intended or not. At several sites, ponds or tailings impoundments are intentionally designed to maximize the rate of cyanide attenuation, and in some cases resultant solutions are suitable for discharge. Advantages of natural attenuation include lower capital and operating costs when compared to chemical-oxidation processes.

Two approaches have been developed to predict the rate of cyanide attenuation in ponds and tailings impoundments. The first method is empirical in nature and uses experimentally derived rate coefficients to estimate the rate of attenuation using a first-order decay equation (Simovic *et al.*, 1985). This approach is relatively simple to apply, but its applicability at a given site must be verified by conducting field testwork and the results may not be accurate under variable weather, water temperature, pond or tailings impoundment geometries, or influent water-chemistry conditions.

The second approach to modelling natural cyanide attenuation was developed by Botz and Mudder (2000). This approach utilizes detailed solution chemical equilibria and kinetic calculations to predict the rate of cyanide losses from ponds and impoundments through a variety of reactions. The reactions of cyanate, thiocyanate, ammonia and nitrate can also be modelled with this approach. This approach can be more time intensive to apply at a given site, but the results are accurate under a wide variety of weather, water temperature, pond or tailings impoundment geometries, or influent water-chemistry conditions.

Examples of natural cyanide attenuation in tailings impoundments are presented in Table 12, as observed at several mines in Australia (MCA, 1996). These data correspond to WAD cyanide reductions ranging from about 55 to 99%, reflective of the varying tailings chemistries, climatic conditions and tailings impoundment geometries at these sites. An additional example of natural attenuation of both cyanide and its related compounds is given in Fig. 4 (Schmidt *et al.*, 1981).

Table 12
Examples of natural cyanide attenuation

WAD cyanide in tailings discharge (mg/L)	WAD cyanide in tailings impoundment decant solution (mg/L)	WAD cyanide reduction (%)
210	94	55
48	10	79
57	0.5	99
150	20	87
125	22	82
186	20	89
82	12	85
99	9	91

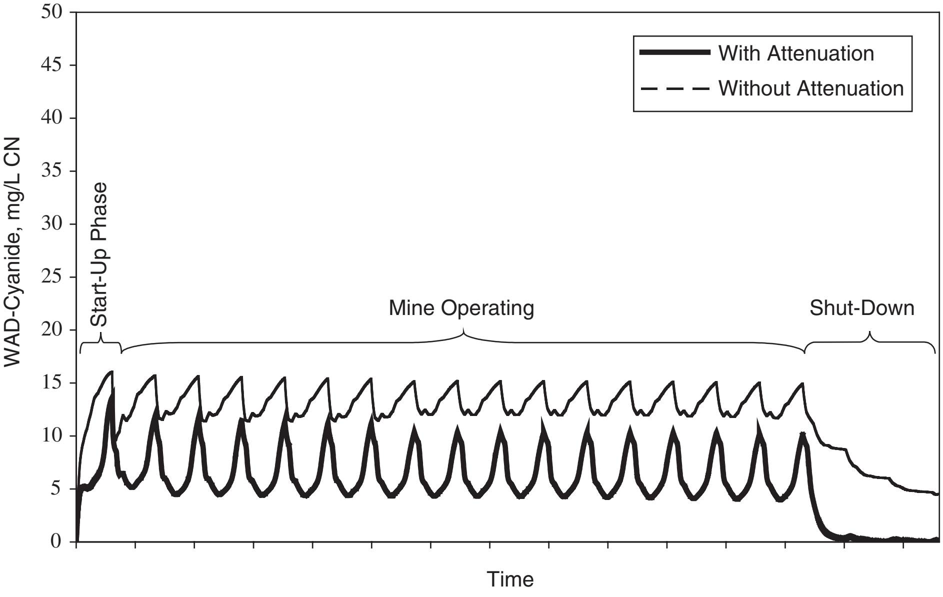

Fig. 4. Example of the natural attenuation of cyanide and related compounds.

Modelling of natural cyanide attenuation is also useful for planning purposes when evaluating a potential mining operation. Results can be used to estimate cyanide levels in a tailings impoundment over the life of the mining operation and into the closure and decommissioning phase. This information is useful from the standpoint of water-management planning, particularly if a water discharge from the site is anticipated to be necessary.

7. TREATMENT OF CYANIDE-RELATED COMPOUNDS

The primary constituents of concern in cyanidation solutions include not only the various forms of cyanide, but the cyanide-related compounds – thiocyanate, cyanate, ammonia and nitrate. In many cases, these compounds are important from a water quality and toxicity standpoint, and low levels must occasionally be achieved in treated waters. The following sections provide general background information on the removal of these cyanide-related compounds.

7.1. Thiocyanate treatment

Thiocyanate (SCN^-) is formed through the interaction of cyanide with sulfur-containing compounds, particularly sulfide minerals such as pyrrhotite [$Fe_{(1-x)}S$], pyrite [FeS_2], chalcopyrite [$CuFeS_2$] or arsenopyrite [$FeAsS$]. As with cyanate, thiocyanate is not a cyanide compound, but is related to cyanide, and is usually only found in solutions that also contain cyanide. Thiocyanate is far less toxic than cyanide and exhibits unique chemical, analytical and treatment characteristics. Thiocyanate removal from decant solution is not routinely practiced in the mining industry, but there are full-scale treatment plants that remove thiocyanate. In the case of biological treatment of cyanide, as well as oxidation with chlorine or ozone, thiocyanate is also removed as part of the process. There are no documented cases of thiocyanate resulting in adverse environmental impacts to aquatic life in the mining industry, but thiocyanate removal may be needed in those cases where land application of the discharge solutions is contemplated, or in plants where bacterial oxidation is practised to liberate gold that is locked in sulfide mineral particles. Bacterial-oxidation plants generally produce high levels of thiocyanate (2–10 g/L) in the downstream cyanidation process. The bacteria used for sulfide-mineral oxidation (*Acidothiobaccilus ferrooxidans*) are vulnerable to even very low concentrations of thiocyanate, so if cyanide-tailings water is recycled to the mill, it must be treated to remove thiocyanate to as low as 1 or 2 mg/L.

Removal of thiocyanate from decant solution can be accomplished with one of several available destruction methods (Mudder and Botz, 2001b). It is possible to chemically or electrochemically regenerate cyanide from thiocyanate (Soto *et al.*, 1996); however, these process have not been implemented on a full-scale basis (Botz *et al.*, 2001). The chemical-destruction methods utilize an oxidant such as chlorine or ozone to convert thiocyanate to cyanide at an alkaline pH, and then cyanide oxidation rapidly continues to yield cyanate, ammonia and nitrate. Several oxidants are capable of oxidizing thiocyanate, but only chlorine and ozone yield suitably rapid reaction kinetics.

Alkaline chlorination and ozone efficiently destroy thiocyanate and are capable of lowering thiocyanate concentrations to a few milligrams per litre. If the residual chloride or chlorine content in treated solution is of concern, then the ozone process may be preferable since ozone dissociates to oxygen or water. Both chlorine and ozone can be used to simultaneously oxidize cyanide, cyanate, and thiocyanate, and often the choice of the appropriate oxidant is based on considerations of cost, by-product generation and process efficiency.

A lower-cost alternative in many cases for thiocyanate destruction is biological treatment. Microorganisms in an aerobic environment readily oxidize thiocyanate and the reactions are rapid at temperatures above about 10–15°C. As with the chemical destruction methods, biological thiocyanate-treatment processes can readily be configured to simultaneously remove cyanide, cyanate, and ammonia along with thiocyanate. At a North American site, a biological treatment plant is used to lower cyanide, cyanate, thiocyanate and ammonia from initial concentrations of about 0.4, 300, 500 and 40 mg/L, respectively, to final concentrations of about 0.08, <5, 0.3 and 0.5 mg/L, respectively (Given *et al.*, 2001). The advantages of biological processes over chemical processes for thiocyanate removal are that capital and operating costs are relatively low and the concentration of reaction by-products is low. However, biological processes are kinetically slow at colder temperatures and do not respond well to rapid fluctuations in solution flow or chemistry.

7.2. Cyanate treatment

Cyanate (OCN^-) is related to cyanide and is often found in waters that contain cyanide. Cyanate originates from the oxidation of cyanide but exhibits different chemical, analytical treatment and toxicity characteristics. Treatment of solutions for cyanate removal is uncommon because it is far less toxic than cyanide, is generally present in metallurgical solutions at low concentrations and does not persist in the environment for long periods of time. In some cases, the cyanate concentration in decant solution may be sufficiently high as to warrant implementation of a cyanate removal process, and typically this is the result of cyanate produced in a cyanide destruction process. This would be limited to situations where decant solution were to be discharged to the environment and the concentration of cyanate in untreated solution would be toxic to aquatic organisms.

The authors are not aware of any full-scale water-treatment facilities operating in the mining industry that specifically target the removal of cyanate or contain a limit on the level of cyanate that can be discharged. However, there are full-scale water-treatment plants that incidentally remove cyanate along with their intended purpose of removing cyanide or other related compounds. Most notable are several biological-treatment plants where processes to remove cyanide, thiocyanate, and ammonia also result in the removal of cyanate. An example is a mine in North America where decant solution is biologically treated for cyanide, thiocyanate, and ammonia removal (Given *et al.*, 2001). These species are removed to low levels in the aerobic treatment system, although the cyanate level is also reduced from about 300 to less than about 5 mg/L.

The biological mechanism of cyanate removal is first the oxidation of cyanate to ammonia, and then ammonia removal proceeds through a biological process termed *nitrification*. Subsequent nitrate removal through a biological denitrification process may also be warranted depending upon the resultant nitrate concentration in solution. Information regarding the removal of ammonia and nitrate through chemical, biological, and physical means is presented later in this chapter.

Cyanate may also be removed from solution using chemical oxidation or hydrolysis processes. Chemical oxidation with chlorine at a slightly alkaline pH will convert cyanate into ammonia, although the chlorination process can easily be configured to complete the oxidation of ammonia into nitrogen gas through a process termed *breakpoint chlorination*. Ozone at an alkaline pH is capable of converting cyanate directly into nitrate, thereby avoiding the intermediate formation of ammonia. The advantage of the ozone process is that the concentration of dissolved species in treated solution is not increased significantly since ozone dissociates into oxygen and water. Cyanate also can be hydrolysed to ammonia at an acidic pH, although the reaction is relatively slow at low temperatures, and in some cases may require solution heating. With the oxidation or hydrolysis reactions, cyanate is converted either into ammonia or nitrate and subsequent removal of these compounds may be required depending upon their resultant concentrations.

7.3. Ammonia treatment

Ammonia (NH_3) is toxic to aquatic organisms, particularly fish, but is usually present in metallurgical streams at low concentrations. The two sources that are responsible for the majority of ammonia that may be present in decant solutions are the following:

- A mixture of ammonium nitrate and fuel oil (ANFO) is often used as a blasting agent at mining operations. A small percentage of ANFO used in blasting will remain unreacted and report as ammonia and nitrate in slurry tailings discharged into a tailings-storage facility. The concentration of ammonia originating from this source is generally low, though in some circumstances ammonia removal from decant solution is required as a direct result of ANFO usage.
- Ammonia is one of the breakdown products of thiocyanate and cyanide oxidation, and forms through the hydrolysis of cyanate in a tailings-storage facility. If cyanate is present in decant solution at an elevated concentration, then often there will be a correspondingly elevated concentration of ammonia.

Through a combination of these two sources, ammonia removal from decant solution is occasionally required at mining operations, particularly if treated solution must be discharged into the environment. Primarily, the concern is with toxicity to aquatic organisms since ammonia is generally not present in decant solution at concentrations that would be toxic to wildlife or waterfowl. If natural attenuation in a tailings-storage facility is not sufficient to limit the concentration of ammonia, then implementation of a decant solution-treatment system may be required for water to be discharged to the environment. Treatment options considered typically include biological, chlorination and ion-exchange processes, though in some cases air stripping may be considered.

Ammonia is readily oxidized through biological nitrification by an aerobic biological-treatment process. This process is practiced at many municipal wastewater-treatment plants throughout the world. The reaction product from this process is first nitrite and then nitrate, which is less toxic than ammonia but may also require removal depending upon its concentration. It is not uncommon for biological-treatment plants to reduce ammonia to concentrations below 1 mg/L; however, applications are generally limited to situations where the solution flow and chemistry do not fluctuate rapidly. Biological conversion of ammonia to nitrate can be conducted at relatively low temperatures, but reactions rates are higher at temperatures above about 10°C.

Ammonia removal through the breakpoint chlorination process converts ammonia directly into nitrogen gas, thereby avoiding nitrate formation as would be encountered with other ammonia-destruction processes. The chlorination process is efficient at removing ammonia to low levels and can also be configured to affect the simultaneous removal of cyanide, cyanate and thiocyanate as well as ammonia. A disadvantage with chlorination, however, is that as ammonia concentrations increase, larger quantities of chlorine may be required, depending upon the solution flow rate. In addition, chlorine added to solution will ultimately convert to chloride and increase the dissolved solids concentration in treated solution. If the concentration of either chloride or total dissolved solids in the treated water is of concern, then alternatives to chlorination should be considered. Chlorine is also highly toxic to aquatic organisms and a dechlorination process must follow any chlorination process used to treat water for discharge to the environment.

In some cases, ion exchange is used to reduce ammonia concentrations without causing a significant increase in the dissolved solids concentration. Ion exchange is also not as prone to process upsets as a result of flow and chemistry fluctuations in comparison to biological treatment processes. Consideration of ion exchange is appropriate when concentrations of interfering species such as sodium, calcium and magnesium are relatively low and when the solution pH is less than about 9.0.

Under these conditions, ion-exchange resins can be selective towards ammonia removal and the process may be economical for full-scale implementation. A significant disadvantage of ion exchange is that resins must be periodically regenerated using concentrated solutions of sodium chloride or sulfuric acid. These solutions along with all ammonia removed from solution will be present in the waste-regenerant solution, and disposal of this waste solution is often difficult and expensive. In addition, ion-exchange resins can become fouled due to the presence of certain dissolved metals in solution, and resin fouling can lead to high costs for purchasing new resin and for disposing fouled resin.

Air stripping of ammonia from solution at a pH above about 11.0 is effective at reducing its concentration and in select applications this process may be economical. For example, if the solution to be treated has a pH near 11.0, then stripping of ammonia can be conducted with little or no initial pH adjustment. The disadvantage arises when the initial pH is below 11.0 and must be adjusted to the alkaline region using lime or sodium hydroxide. This adds to the cost of the process and increases the concentration of dissolved solids in the treated solution. In addition, if the pH of stripped solution must be lowered to less than 9.0 before being discharged into the environment, then sulfuric acid addition may be required. This also adds both to the cost of the process and to the concentration of dissolved solids in treated solution. Scale formation in process equipment may also be problematic due to carbondioxide absorption from atmospheric air, which will occur at elevated solution pH values. Because of these drawbacks, ammonia stripping is limited to applications when other treatment approaches would not be feasible or economical.

7.4. Nitrate treatment

Nitrate (NO_3) is a relatively non-toxic compound at the concentrations typically observed in decant solutions, and usually is not of concern relative to wildlife, waterfowl or aquatic organism toxicity. The primary concern with nitrate is generally related to drinking waters, where elevated nitrite and nitrate concentrations can be harmful to humans, particularly young children and infants. In addition, nitrate is a biological nutrient and in some cases can lead to accelerated algae growth in waters, thereby consuming dissolved oxygen and impairing the ability of fish to survive. Nitrate is a relatively stable compound in surface waters and because of this, its removal from waters discharged to the environment is often required. There are relatively few treatment technologies that can be implemented on a full-scale basis to reliably lower nitrate levels, though the few that are available are effective and economic in many cases.

The most widely applied nitrate treatment technology is biological denitrification, which proceeds under anoxic conditions. In this process, nitrate is converted to nitrogen gas, which is then vented to the atmosphere. Like most biological processes, denitrification is best suited for situations where the solution flow and chemistry do not fluctuate rapidly and where the solution temperature is above about 10–15°C. The process does not significantly increase the concentration of dissolved solids, but does require the addition of a supplemental carbon source such as methanol or molasses. A key advantage of biological denitrification is that it can be coupled with an aerobic biological process to affect the removal of cyanide, cyanate, thiocyanate, ammonia and nitrate. Under many circumstances, biological treatment systems are inexpensive to construct, operate and maintain and will provide high-quality effluent.

Ion exchange can also be used to remove nitrate to low levels, but as described for ammonia removal, the disadvantages of waste-brine disposal and resin fouling have limited its application in the mining industry. Under conditions where the concentration of interfering compounds such as chloride and sulfate are relatively low, ion exchange may be an economical approach.

8. EFFLUENT STANDARDS

The three basic design criteria related to considering a water or tailings-treatment application are:

- the flow of untreated water or tailings;
- the chemistry of untreated water or tailings; and
- goals for treated effluent quality.

The first two of these criteria are an outcome of proper consideration of the site water-balance coupled with consideration of the chemical behavior of each water-containing stream. The third criterion is often less defined in early stages of planning but often has the most influence with respect to selecting candidate treatment processes.

Goals established for treated effluent quality are normally selected to protect human health, terrestrial wildlife and/or aquatic life. For human health protection, drinking-water standards may be considered, either those established locally, nationally or internationally. The World Health Organization (WHO) drinking water standard for cyanide is 0.07 mg/L measured as total cyanide. This compares to the US Environmental Protection Agency (US EPA) drinking water standard of 0.2 mg/L measured as total cyanide. There are numerous additional drinking water standards for metals and other inorganic and organic constituents that must be considered in addition to cyanide.

For terrestrial wildlife protection, migratory waterfowl are often the most sensitive of species that are to be protected. In this case, the concentration of cyanide in open process ponds and tailings impoundments must be maintained at an acceptable level. The acceptable level is normally considered to be less than 50 mg/L measured as WAD cyanide. In cases where maintaining this level of cyanide would not be practical, such as in heap-leach ponds, netting or other exclusion techniques should be considered to prevent contact by wildlife.

With respect to cyanide, aquatic life protection leads to the most stringent of effluent standards due to the relatively high sensitivity of fish and other species to cyanide. The toxicological form of cyanide in this case is normally WAD cyanide, and recent trends worldwide have been to regulate the levels of WAD cyanide in receiving waters to protect aquatic life. In-stream guidelines published by the US EPA for the protection of freshwater aquatic life are 0.022 and 0.0052 mg/L, both stated in terms of free cyanide. However, the US EPA and other regulatory agencies realize that the measurement of free cyanide at this level is not currently possible at the commercial scale; therefore, the more conservative approach of measuring WAD or total cyanide is commonly adopted. However, the statistical significance of cyanide measurements at these low levels using current techniques is debatable. Depending on the level of dilution available in the receiving water, the required level of effluent treatment can be determined. The US EPA also has published guidelines for protection of aquatic life in seawater.

In some cases, adoption of site-specific standards for cyanide should be considered, both to ensure the protection of receiving ecosystems and to avoid adopting overly stringent effluent standards. The US EPA aquatic life guidelines were developed according to the most sensitive of aquatic species, but are not necessarily guidelines that should be directly adopted at a specific mine site. At many sites, aquatic species considered by the US EPA may not be present in the receiving water, and the toxicity of cyanide to other more or less sensitive aquatic species may warrant consideration. This approach has been taken at several mine sites where in-stream, site-specific WAD cyanide standards were established in the range of 0.08–0.10 mg/L for protection of freshwater aquatic life (Russell *et al.*, 2000; Mudder *et al.*, 2001).

9. SUMMARY

There are several water and tailings treatment processes that have been successfully used worldwide for cyanide removal at mining operations. The key to successful implementation of these processes involves consideration of the following:

- Site water and cyanide balances under both average and extreme climate conditions.
- Goals to be adopted for cyanide levels in treated effluent, including the form of cyanide to be regulated (free vs. WAD vs. total cyanide).
- The range of cyanide treatment processes available and their ability to be used individually or in combination to achieve treatment objectives.
- Proper treatability testing, design, construction, maintenance and monitoring of both water- and cyanide-management facilities.

By carefully considering these aspects of water and cyanide management before, during and after mine operation, operators can reduce the potential for environmental impacts associated with the use of cyanide.

Another aspect of cyanide treatment to be considered is the potential environmental impact of the cyanide-related compounds – cyanate, thiocyanate, ammonia, nitrate and nitrite. These compounds may be present in mining solutions to varying extents and may require treatment if water is to be discharged. Each of these cyanide-related compounds is affected differently in the treatment processes discussed, and this should be considered when evaluating cyanide-treatment alternatives for a given site.

Table 13
Preliminary guide to selecting cyanide treatment processes

Treatment process	Iron cyanide removal	WAD cyanide removal	Slurry application	Solution application
SO_2/air	✓	✓	✓	✓
Hydrogen peroxide	✓	✓		✓
Caro's acid		✓	✓	
Alkaline chlorination	✓	✓		✓
Iron precipitation	✓	✓	✓	✓
Activated carbon	✓	✓		✓
Biological	✓	✓		✓
Cyanide recovery		✓	✓	✓
Natural attenuation	✓	✓	✓	✓

Table 13 provides a simplified summary of the general applications of various treatment technologies for the removal of iron cyanide and WAD cyanide. This table represents a very simplified summary, but can be used as a conceptual screening tool when evaluating cyanide-treatment processes.

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Chapter 29

Cyanide recovery

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Several processes are now available for the recovery of free and weak-acid dissociable (WAD) cyanide from gold-plant solutions and pulps, including both commercial processes and processes that are still in the development phase. In the past, the incentive for evaluating cyanide recovery in gold-plants has been economic. In many cases, it has been possible to demonstrate (at least in the laboratory and on paper), an improvement in process economics by:

- reducing the costs of tailings detoxification;
- recycling cyanide at lower cost than the purchase/delivery price of new cyanide; and
- generating additional revenue via by-product sales.

Despite a number of convincing case studies, few cyanide recovery plants have been built at operating gold mines.

There is arguably an even more compelling reason for mining companies to consider recycling cyanide today. The use of cyanide in the mining industry is attracting a growing storm of negative public opinion following several highly publicized spills over the last couple of years, and government regulations controlling the discharge of cyanide from metallurgical plants are being tightened. The widely accepted limit of 50 mg/L WAD cyanide entering a tailings impoundment is becoming accepted as ‘best practice’ in the worldwide gold industry, and the World Bank, as well as the International Finance Corporation, will include this level or lower in their new guidelines for financing gold projects. The European Union has also proposed new waste management guidelines for the mining industry, with a sliding scale for WAD

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cyanide entering tailings impoundments going from 50 to 25 mg/L in 5 years, to 10 mg/L in 10 years. Treatment to lower CN levels entering impoundments is mandatory in most regions of the world today. It may already be too late for the gold industry to claim the high ground as far as cyanide management is concerned, but the time has come to demonstrate improved environmental stewardship in the use of this commodity that is so vital for their industry. There is little doubt that the widespread implementation of cyanide recycling will reduce the impact of the cyanidation process on the environment, both by reducing the risk of spills (with less cyanide being transported from manufacturing plants to gold mines) and by reducing the loading of toxic and non-toxic metals and ions in the tailings.

The pros and cons of the different processes that are available for the treatment of gold and silver plant tailings to recover cyanide for recycling are presented in this chapter, along with a techno-economic argument for the incorporation of this technology into many gold-plant flowsheets today.

1. INTRODUCTION

There has been growing interest in cyanide recovery from gold and silver plant tailings throughout the gold mining industry over the last few years. This interest has been spurred by two factors. First, the increasing cost of destroying cyanide to levels that must meet stringent regulations for tailings impoundment or discharge to the environment. Second, many gold ore bodies suffer high cyanide consumption costs as a result of the presence of base metals (principally copper) that react with and consume cyanide during the gold leach. The cost of recovering and recycling this cyanide from the tailings will often be lower than the cost of purchasing new cyanide. When this cost benefit is added to the reduced cost of tailing's detoxification, a strong economic case can frequently be made for cyanide recovery.

The greatest economic benefit will be realized in gold/silver plants where excess cyanide is needed during leaching, either to drive the leaching kinetics (for example, in the treatment of gold ores containing sufficient quantities of silver minerals) or to account for high cyanide consumption and the formation of WAD metal-cyanide species (in particular, the formation of copper cyanide complexes). At each of the currently or recently operating cyanide recovery plants around the world, all of which use the acidification–volatilization–regeneration (AVR) process (see below), overall cyanide consumption has been reduced by about one-half, and final tailings cyanide concentrations have been reduced to less than 30 mg/L.

A number of processes for recovering cyanide from gold-plant barren solutions or pulps have been developed. In most cases, cyanide is recycled by first converting it from the free or WAD complexed form in which it exists in gold-plant tailings, to hydrocyanic acid gas (HCN). The negative public perception about this highly toxic gas, and concerns about the ability of the mining industry to handle it safely in a processing plant, have probably presented the greatest impediments to implementation of these processes. In this regard, the mining industry can gain confidence from the few gold-plants that have already introduced cyanide recovery technology, and from the chemical industry, which handles large quantities of HCN gas routinely and safely.

2. THEORETICAL BACKGROUND

If the cyanide is present in the tailings as free cyanide ($\mathrm{p}K_\mathrm{a} = 9.4$), it is possible to convert $>99\%$ of the cyanide into HCN gas by lowering the pH of the tailings to about 7:

$$\mathrm{CN^- + H^+ \rightarrow HCN} \tag{1}$$

If, on the other hand, the cyanide is present as a metal-cyanide complex, the pH must be reduced to more acidic values (which vary with the strength of the complex) to break down the complex and produce HCN gas. For example, the weak zinc-cyanide complex ($\log \beta_4 = 17.4$) breaks down completely at about pH 5, producing zinc sulfate as an aqueous-soluble species, plus 4 moles of HCN gas:

$$\mathrm{Zn(CN)_4^{2-} + 2H_2SO_4 \rightarrow ZnSO_4 + 4HCN + SO_4^{2-}} \tag{2}$$

The copper cyanide complex does not break down completely, even in strong acid solution, unless there is an oxidant present in the solution. In the absence of oxidant, the copper tricyanide species (which is the most stable copper complex under normal cyanidation conditions: $\log \beta_3 = 28$) decomposes to form a CuCN precipitate, plus 2 moles of HCN gas, at pH values less than 3. Hence, 33% of potentially recoverable cyanide is lost to the precipitate:

$$\mathrm{Cu(CN)_3^{2-} + 2H^+ \rightarrow CuCN + 2HCN} \tag{3}$$

The nickel tetracyanide complex ($\log \beta_4 = 30$) also requires a pH value of less than 3 to break down and liberate HCN gas, with a reaction stoichiometry the same as that shown for zinc in Eq. (2). However, the very strong ferrocyanide ($\log \beta_6 = 35$), ferricyanide ($\log \beta_6 = 44$) and cobalticyanide complexes ($\log \beta_6 = 64$) do not break down, even in strong acid solutions, without destruction of the cyanide.

In situations where both ferrocyanide and cuprous cyanide are present in the same cyanide leach liquor (which frequently occurs with high cyanide-consuming ores), treatment of the solution with acid to pH <4 produces a double metal cyanide precipitate such as $Cu_2Fe(CN)_6$ or $Cu_4Fe(CN)_6$:

$$4Cu(CN)_3^{2-} + Fe(CN)_6^{4-} + 12H^+ \rightarrow Cu_4Fe(CN)_6 + 12HCN \tag{4}$$

The $Cu_4Fe(CN)_6$ species is formed under oxygen-starved conditions in solution, whereas $Cu_2Fe(CN)_6$ is formed in a well-aerated solution. From the stoichiometry of Eq. (4), it can be seen that the ferrocyanide molecule releases the third molecule of CN from the copper *tri*cyanide complex, so the presence of ferrocyanide results in increased recovery of cyanide from the copper–cyanide species. The analogous zinc–iron double metal cyanide complex, $Zn_2Fe(CN)_6$, is formed under acidic conditions when zinc tetracyanide and ferrocyanide are present in solution.

When both copper cyanide and thiocyanate anions are present in the cyanide leach solution, which frequently occurs during leaching of gold ores that contain reactive copper sulfide minerals, the following reaction takes place, in addition to the reactions shown in Eqs. (1), (3) and (4):

$$Cu(CN)_3^{2-} + SCN^- + 3H^+ \rightarrow CuSCN + 3HCN \tag{5}$$

The solubility product of the CuSCN species ($K_{sp} = 1.8 \times 10^{-13}$) is higher than that of the CuCN species ($K_{sp} = 3 \times 10^{-20}$), which means that CuCN formation (Eq. (3)) should be favoured over CuSCN formation (Eq. (5)). However, at low pH values ($pH \leqslant 2$) and low HCN concentrations (as in the AVR process), reaction (5) is favoured over reaction (3). A cyanide regeneration process that is based on the CuSCN chemistry shown in Eq. (5) has been described by Soto *et al.* (1996). There are several important advantages of a process utilizing the CuSCN precipitation chemistry (Eq. (5)) over the chemistry shown in Eqs. (3) and (4):

- Firstly, all three molecules of CN per molecule of copper are released for recovery and recycling, versus two molecules of CN in the CuCN process.
- Secondly, the precipitate contains no cyanide, which would make it a more acceptable feed if it were to be sold to a smelter.
- Finally, the process provides a bleed for thiocyanate, which would otherwise report to the final tailings and could potentially become an environmental problem.

As an alternative to the reaction shown in Eq. (5), for situations where there is insufficient ferrocyanide or thiocyanate in solution ($Cu \gg SCN$), it is possible to achieve the same objective by adding sulfide ions to the cyanide leach solution. In this case, the formation of cuprous sulfide (or synthetic chalcocite) is favoured because of its extremely low solubility

($K_{sp} = 2.3 \times 10^{-48}$). The following reaction takes place:

$$2\mathrm{Cu(CN)}_3^{2-} + \mathrm{S}^{2-} + 6\mathrm{H}^+ \rightarrow \mathrm{Cu_2S} + 6\mathrm{HCN} \qquad (6)$$

This reaction is irreversible at pH <4 and takes place quantitatively with stoichiometric additions of sulfide ions and acid. Eq. (6) forms the chemical basis of both the Sulfidization–Acidification–Recycling–Thickening (SART) process (MacPhail *et al.*, 1998), which is described in more detail below, and the Metallgeseltshaft Natural Resources (MNR) process (Potter *et al.*, 1986).

From the foregoing discussion, it is apparent that the optimum pH for cyanide liberation from gold and/or silver plant tailings will vary from plant to plant, and will depend on the cyanide speciation in solution.

3. PRACTICAL CONSIDERATIONS

An important consideration when deciding how to treat the gold or silver plant tailings for cyanide recovery, is whether to treat the tailings directly as a slurry, or to first separate the solids and liquids and treat only the liquid phase. In making this decision, the following factors must be taken into consideration:

- The cost of solid/liquid separation may be substantial. If the solids and liquids have already been separated (in a Merrill–Crowe or heap-leach operation, for example) this is not a factor. If they have not been separated (in a carbon-in-pulp (CIP) or carbon-in-leach (CIL) operation, for example), the cost of solid/liquid separation must be included as part of the cost to recover cyanide. This could be significant, particularly for high clay content, slimy ore. In most cases, the final washed solids will still have to be treated by a detoxification process to remove residual soluble cyanide species.
- Cyanide recovery by acidification of the tailings, followed by volatilization and reneutralization of the HCN gas (known as the AVR process) is faster and more efficient from solution than from pulp, requiring lower volumes of air flow per unit volume of tailings treated and smaller equipment. Capital costs per unit volume of tailings feed are therefore lower for an AVR plant treating solution than for one treating pulp. In addition, attempts to implement the AVR process on tailings slurry have been dogged by scaling problems, such as encountered at DeLamar Mine in Idaho, USA, and the Cerro Vanguardia plant in Argentina (Radcliffe, 2000). In both these cases, the plants were originally built to handle tailings slurry, but were subsequently converted into solution treatment due to severe scaling.

- Operating costs are lower for cyanide recovery plants treating solution than those treating pulp. The main operating cost is the sulfuric acid that is consumed in lowering the pH to the desired final pH value. When treating solutions, this consumption is close to stoichiometric, based on Eqs. (1)–(6) (*i.e.*, half a mole of sulfuric acid per mole of CN, or approximately 2 : 1 on a mass basis). When treating pulp, the acid consumption can be 2–10 times higher, depending on the final pH required and the acid-consuming constituents in the ore.
- When the main source of cyanide consumption is the reaction to form copper–cyanide complexes in solution (as is frequently the case), an added benefit of treating solution rather than pulp is the opportunity afforded to recover and sell the copper precipitate. The sale of by-products should have a positive impact on cyanide recovery economics.

Despite the many positive attributes of treating solutions rather than pulps, the cost and inefficiencies of solid/liquid separation will render cyanide recovery from solution unattractive in some cases. In these situations, resin-in-pulp (RIP) processes are the best alternative, and examples of this technology are discussed below. In fact, ion-exchange technology should always be considered, even when treating solution for cyanide recovery, because the resin processes will usually upgrade the strength of the cyanide solution 20–50-fold prior to acidification/precipitation. This in turn will lower the capital cost and improve worker health and safety in the final cyanide regeneration steps of the process. In some cases, the cyanide strength in the eluate from an ion-exchange process will be sufficiently high for direct recycling to leach, circumventing the need for volatilization of HCN.

The decision on whether or not to pre-concentrate by volatilization is based on the water balance in the plant. If pre-concentration is unnecessary, or is achieved by ion exchange, circumventing volatilization results in a simpler, safer and lower cost plant.

Although not considered in this chapter, a flowsheet in which cyanide is recovered after gold leaching and before gold extraction on activated carbon may warrant attention in the future. Laboratory studies (Fleming and Nicol, 1984) have shown that the kinetics and equilibrium loading of gold cyanide on activated carbon are enhanced very significantly by lowering the cyanide strength and the pH of solution (both of which would occur as a result of cyanide recovery). This was confirmed during installation of the Cyanisorb Process at the Golden Cross mine in New Zealand. Incorporation of the AVR plant after leaching and before CIP was tested, and was found to enhance gold recovery by several percent (Mudder, 2004).

4. PROCESS ALTERNATIVES

4.1. Direct recovery without preconcentration, by tailings-solution recycling

In order to ensure good leaching kinetics and high overall gold recovery, it is always necessary to add more cyanide during leaching than will be consumed in the leaching process. This excess cyanide reports to the tailings as uncomplexed or free cyanide, and it is often possible to recycle a portion of this cyanide at fairly minimal cost. A number of gold-plants around the world have adopted this approach.

The basic requirements to achieve this objective are firstly to recycle solution rather than slurry and, secondly, to satisfy an overall water balance in the plant. These requirements are met quite naturally in a heap-leach operation, where the residual cyanide in the pregnant solution emerging from the bottom of a heap is recovered by simply recycling this solution (after gold and/or silver recovery) back to the top of the heap. It is not so simple in a milling operation, but some of the residual free cyanide can be recovered by thickening the mill slurry prior to leaching, and again thickening the leach plant tailings prior to discharge. For example, if the feed and discharge from cyanidation and gold recovery can be thickened to 60% solids, and the leach/gold recovery operation is conducted at 40% solids, the net result is that about half of the free cyanide in the tailings is recovered and recycled. This is depicted schematically in Fig. 1.

Pros

- The process is simple with relatively minor capital cost (two thickeners, larger leach and CIP tanks) and minimal operating costs.
- The process does not require conversion of free cyanide to HCN gas.

Cons

- It is difficult to recover more than ~50% of the free cyanide in the tailings. The remaining tailings must still be treated by a detoxification process prior to discharge to the environment.
- The cyanide present in tailings as WAD metal cyanide is not recovered without additional processing.

4.2. Direct recovery by the SART process

The SART process was developed in the late 1990s (MacPhail *et al.*, 1998), and is similar to the previous process, in that there is no pre-concentration of cyanide. SART should be applied in those situations where there is a

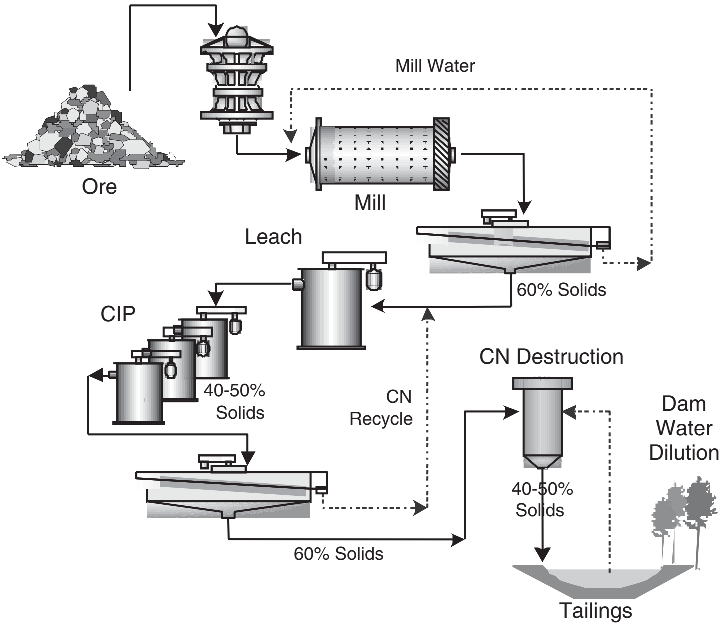

Fig. 1. Simplified flowsheet for direct recovery of free cyanide from gold-plant tailings.

significant concentration of copper (or zinc) as WAD cyanide complexes in the tailings (or recirculating heap-leach liquor). Metals are precipitated from solution by the addition of sulfuric acid (typically to pH 4–5) and sulfide ions, as depicted in Eq. (6). The precipitate is recovered by thickening and filtration, and the liquor is neutralized and recycled to leach. The concentration of free cyanide in the recycle solution is essentially the same as the combined concentrations of free and WAD cyanide in the feed to the SART process.

The solids density in the primary reactor will usually be very low (in the 0.05–0.5% range), and therefore it is beneficial to thicken the precipitate prior to filtration. This also affords the opportunity to pump a portion of the thickener underflow back to the primary reactor, where it can act as seed material for new precipitate formation. With appropriate recycling and flocculation, solids densities of 10–15% can be produced in the thickener underflow, which reduces the volumetric flowrate to the pressure filter by a factor of 100 or more. A schematic flowsheet is shown in Fig. 2.

The basic chemistry of the SART process is identical to the MNR process, which was extensively tested in the 1980s (Potter *et al.*, 1986). The fundamental difference between the two processes lies in the physical handling of the precipitate. In the MNR process, the Cu_2S precipitate is pumped directly from the primary reactor to a pressure filter as a low-density slurry. In the

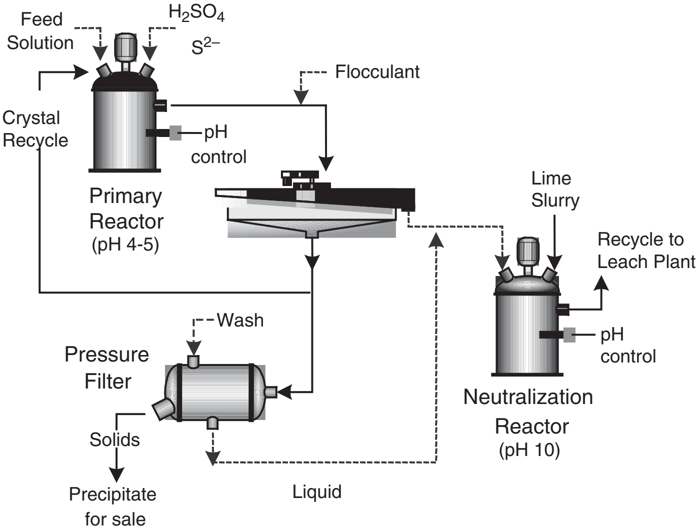

Fig. 2. SART process flowsheet.

SART process, the volume of slurry reporting to the pressure filter is decreased by up to 99%, greatly reducing filter plant costs and improving the safety aspects of this potentially hazardous unit operation. Both the MNR and SART processes have been piloted, and a full-scale SART plant was built and successfully commissioned at Newcrest's Telfer operation in Western Australia in ~2001.

The experience gained during several laboratory programmes and one pilot-plant SART campaign can be summarized as follows:

- When the predominant WAD cyanide complex in the tailings is copper (which is generally the case), the SART process produces a precipitate of almost pure Cu_2S, analysing ~70% Cu and ~20% S. There is usually minimal cyanide in the precipitate (<0.15%).
- Ferrocyanide and thiocyanate are not precipitated at all, and these species build up in the recirculating solution phase. They can be precipitated and removed from a bleed stream by lowering the pH to about 2 (without sulfide addition). Because of the high stability of the ferrocyanide ion, the cyanide that recycles in the form of this complex does influence gold cyanidation.
- The copper precipitation reaction rate is fast (<5 min) and the precipitate flocculates readily (with appropriate flocculant addition) and settles rapidly, producing a fairly dense thickener underflow (10–15% solids) and clear overflow.

- The amount of sulfide added (as NaSH) should be stoichiometric, based on the formation of Cu_2S. In a 3-week continuous pilot-plant campaign, in which cyanide recovery by the SART process was integrated with leaching and CIP, sulfide addition at 90–100% of the stoichiometric amount was found to be adequate for stable operation (MacPhail *et al.*, 1998).
- If there is any zinc in the tailings, it will be co-precipitated (as ZnS) with the copper sulfide.

The pros and cons of the SART process are expected to be essentially the same as the direct recycling approach, with the added advantage that revenue can be generated from the sale of high-grade copper (or zinc) sulfide precipitates. However, this process has only enjoyed a few months of full-scale operation (at Newcrest Mining's Telfer operation in Western Australia), so accurate comparisons are difficult to make.

4.3. Direct recovery by the AVR process

The earliest experience in the mining industry with cyanide recovery from tailings was the AVR process, which was practised at the Pachuca silver mine in Mexico and at the Flin Flon Mine in Manitoba, Canada (Davis *et al.*, 1946; Flin Flon Mill Staff, 1946) almost 60 years ago. The modern version of AVR is known as the Cyanisorb process, and it has been installed at the Golden Cross Mine in New Zealand, the DeLamar Mine in Idaho, USA, the Rio Paracatu Mine in Brazil, and the Cerro Vanguardia Mine in Argentina (Botz and Mudder, 1998). Only the two South American mines are currently operating.

The AVR process involves acidification of the gold plant-tailings with sulfuric acid, to lower the pH from ~ 10 to <7. If the tailings contain WAD cyanide complexes, then it is necessary to lower the pH to between 3 and 5, as discussed in the Section 2. The process can be applied to solutions or pulps, although solution treatment is preferred in most cases for the reasons outlined above. During acidification, free cyanide and relatively weakly complexed cyanide (complexes of Zn, Cd, Ni, Cu) are converted into HCN gas, which is then volatilized by passing a stream of air bubbles through the tailings pulp or solution. The traditional AVR process used low pH in shallow stripping basins, which required massive air flows and energy consumption to effectively volatilize the HCN. The modern (Cyanisorb) process matches the operating pH to the cyanide species in the tailings, and uses low pressure air at low flow rates through a tall stripping tower. The tower is baffled with plates or packed with inert media to improve gas/gas contact.

The air/HCN gas stream is scrubbed in a caustic solution in a second tower reactor to convert the HCN back into free cyanide ions for recycling. Scrubbing in a lime scrubber has been attempted, but has not been installed at any of the operating plants, mainly owing to concerns about scaling. It is possible to build up the cyanide concentration in the scrubber to the solubility limit of the sodium or calcium cyanide salt, although a practical limit of ~100 g/L CN is usually used.

The traditional AVR process has been described by Riveros *et al.* (1993) and the Cyanisorb Process has been described by Stevenson *et al.* (1998).

The experience gained from several unpublished laboratory and pilot campaigns over the years at SGS Lakefield Research, treating widely divergent feed materials, can be summarized as follows:

- The rate of conversion of free and complexed cyanide into HCN as well as the precipitation of metals is rapid (<10 min), whereas the rate of stripping of HCN from the solution to the gas phase is relatively slow (several hours for complete stripping). The HCN stripping rate can be enhanced in a well-designed stripping tower, but will always be the rate-determining step in the process. Stripping rates can be enhanced significantly by heating the tailings, although this cost would be prohibitive unless waste heat was available.
- Given sufficient residence time in the HCN stripping reactor, the AVR process is capable of producing final effluents that are very low in cyanide and metals (CN_{TOT}, Cu, Fe <1 mg/L). In contrast to the SART process, iron precipitates completely (and copper partially) at a pH of <4, presumably as $Cu_4Fe(CN)_6$. It is necessary to lower the pH to ~3 to precipitate the remaining copper as CuCN. At a final pH of $\leqslant 2$, SCN precipitates as CuSCN, if there is sufficient copper left in solution.
- When treating solutions, the acid consumption is close to stoichiometric, based on total cyanide in solution. In one campaign in which solutions and pulps from the same operation were tested, acid consumption was five times higher for pulp treatment than for solution treatment. The rate of HCN stripping from pulp was also significantly slower than from solution (Fleming, 2001).

Botz and Mudder (1998) have developed operating and capital costs estimates for a generic silver plant in the USA, treating 1 million tons of ore annually, and using the Cyanisorb AVR Process to recover cyanide at a concentration of 300 mg/L WAD cyanide from the tailings. The capital cost of the plant was ~$5 million and the operating costs were about $1.00/kg of NaCN recovered. Not only was this cost lower than the cost of new cyanide delivered to the plant ($1.30/kg NaCN), but the cost of cyanide destruction (reported to be in the range $0.50–1.00/kg NaCN) was avoided. The payback time on the capital investment was less than 2 years. These capital and operating costs are in the same range as those reported for the Cyanisorb plant at the Delamar Mine in USA (Stevenson *et al.*, 1998).

Pros

- The AVR process has been studied and practised for many years, and the practical and theoretical aspects are well understood.
- It is the only process involving HCN generation that has been applied commercially in the mining industry, with a wealth of experience gained from several operating plants around the world.
- In cases of high cyanide concentration in the tailings, the process has lowered the overall operating costs in those plants where it has been installed.

Cons

- The process may not be well suited to the treatment of slurries in many cases, because of (a) the potential for high acid consumption if there are oxide/carbonate minerals in the ore and (b) the potential for severe scaling problems. In addition, HCN stripping rates are somewhat slower from slurry than solution
- It is difficult to achieve very low values of residual cyanide in the treated solution in practice, and supplementary cyanide detoxification may be required.

4.4. Indirect recovery with preconcentration by ion-exchange resins

It is often inconvenient, costly or inefficient to recover cyanide directly from gold-plant tailings. This is the case if the tailings pulp is difficult to separate into solid and liquid components (as occurs with laterite, high-clay content, slimy or viscous ores) and also if the tailings solids are high acid-consumers. Under these situations, direct acidification of the tailings results in high operating costs as a result of high acid consumption and inefficient cyanide and copper recovery due to the loss of CuCN precipitate to the tailings. Air stripping of HCN from slurry is also inefficient, requiring long residence time in the stripping column and high air flowrates.

Anion-exchange resins can play a valuable role in these situations, as first pointed out by Goldblatt in the 1950s (Goldblatt, 1956, 1959). The (RIP) process is well developed in the mining industry for other applications (uranium and gold recovery), and presents the opportunity to recover cyanide directly from pulp tailings, circumventing solid/liquid separation processes. Moreover, conventional, commercial strong-base resins are well suited to this application.

The most common cyanide species in gold-plant tailings are free cyanide anions (usually 100–200 mg/L) as well as the cyano complexes of copper, zinc, iron, and sometimes nickel.

The free cyanide anion has a low affinity for anion-exchange resins, and can only be extracted efficiently after all the metal-cyanide complexes, plus most other anions (especially thiocyanate), have been extracted. However, free cyanide can be efficiently extracted if it is pre-complexed with a metal ion such as zinc (or copper) prior to ion exchange, as discussed below.

The ability of anion-exchange resins to efficiently extract copper, zinc, and nickel cyanide, as exemplified in the adsorption isotherms shown in Fig. 3, presents an opportunity to recover these complexes when they are present in the tailings of a gold-plant.

Nickel cyanide is uncommon in gold-plant tailings, while cobalt (III) and iron cyanides form such stable complexes that it is impossible to break them down without simultaneously destroying the cyanide ion. Thus, while these complex anions can be extracted from gold-plant tailings by ion exchange, thereby meeting modern standards for total cyanide and making the tailings amenable for direct discharge to the environment, they do not yield their cyanide for recycling.

Processes have been developed in the laboratory and in small pilot plants to recover cyanide as the zinc and copper cyanide complexes, via ion exchange.

4.4.1. *Cyanide recovery by RIP using zinc complexation (zinc cyanide process)*

Zinc cyanide is found naturally in many gold leach circuits, particularly those employing the Merrill–Crowe process for final gold recovery. In

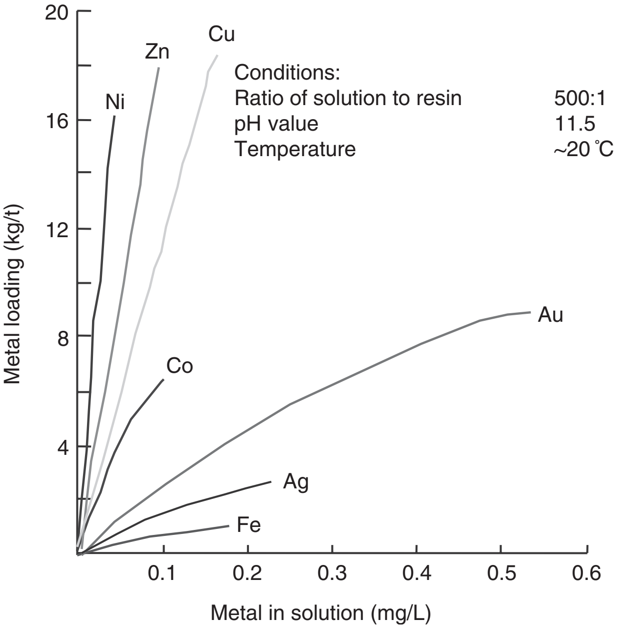

Fig. 3. The equilibrium loading of various metal cyanide complexes from a plant leach liquor onto a strong-base resin, A101Du (after Fleming and Cromberge, 1984).

addition, a zinc salt can be added to the leach tailings to pre-complex all of the free cyanide as the zinc cyanide WAD complex. Although this complex is the weakest of the WAD cyanide complexes $Zn(CN)_4^{2-}$, $\log \beta_4 = 17.4$), it has a very strong affinity for anion-exchange resins, as shown in Fig. 3.

Zinc cyanide loads onto a strong base anion-exchange resin via the following stoichiometry:

$$(\circledR\text{-}\overset{+}{N}R_3)_2\ SO_4^{2-} + Zn(CN)_4^{2-} \rightarrow (\circledR\text{-}\overset{+}{N}R_3)_2\ Zn(CN)_4^{2-} + SO_4^{2-} \tag{7}$$

where the symbol ® represents the resin's polystyrene backbone and R represents an alkyl group. The stoichiometry of Eq. (7) shows that each resin functional group effectively loads two cyanide ions. Therefore, not only does the pre-complexation reaction convert cyanide from the poorly loading free-cyanide form into the strongly loading zinc–cyanide complex form, it also doubles the total loading capacity of the resin for cyanide ions. Resins are capable of loading close to their theoretical capacity (30–40 g/L zinc, 50–65 g/L cyanide) from quite dilute zinc cyanide solution (< 100 mg/L Zn), and are able to produce very low levels of cyanide in the final effluent (< 1 mg/L). Pre-complexing the free cyanide with zinc cations therefore has the potential to produce high loading of cyanide on the resin (2–2.5 mol CN/L) and very low concentrations of free and WAD cyanide in the tailings.

Once the resin is fully loaded, it is transferred to elution, where it is treated to recover cyanide and restore the resin loading capacity so that it can be recycled to the RIP process. To elute the zinc cyanide, the loaded resin is treated with sulfuric acid, which breaks down the zinc cyanide complex completely, producing zinc sulfate and HCN gas in solution (as depicted in Eq. (2)). If the acid solution (100–150 g/L H_2SO_4) and the resin are moved countercurrent to one another, it is possible to produce a strong HCN solution (> 5% HCN) containing very little excess acid (pH 4–5), such that the eluted resin is left loaded with sulfate rather than *bi*sulfate anions (Eq. (8)). This is an economically important requirement, because the acid consumed in elution increases by 50% when the resin is converted into the *bi*sulfate form:

$$\begin{aligned}(\circledR\text{-}\overset{+}{N}R_3)_2\ Zn(CN)_4^{2-} + 2H_2SO_4 \rightarrow\ & (\circledR\text{-}\overset{+}{N}R_3)_2\ SO_4^{2-} \\ & + ZnSO_4 + 4HCN\end{aligned} \tag{8}$$

It is necessary to separate the $ZnSO_4$ and HCN in the strip liquor, so that the zinc can be recycled to the pre-complexation reaction. This would be done by AVR. The HCN gas is volatilized from the regenerant solution in a stream of air, which is scrubbed in lime or caustic solution to recover the cyanide as the usable free cyanide ion (Eq. (9)). Because of the high concentration of HCN in the regenerant solution (10–50 g/L), the size of the stripping column will be relatively small compared to an AVR plant treating tailings solution directly, and the HCN stripping process should be fast and efficient:

$$2HCN + Ca(OH)_2 \rightarrow Ca(CN)_2 + H_2O \tag{9}$$

The barren regenerant solution can be recycled directly to the pre-complexation reactor, or it can be treated with lime or caustic to precipitate zinc hydroxide for sale, discard or recycling. A simplified flowsheet of this process is shown in Fig. 4.

The only reagents theoretically consumed are sulfuric acid (stoichiometric consumption: 0.5 mole per mole of cyanide recovered, or 1 kg H_2SO_4/kg NaCN) and lime (stoichiometric consumption: 0.5 mole per mole cyanide, or 0.75 kg $Ca(OH)_2$/kg NaCN).

A fairly basic operating cost comparison for recycling cyanide (from the free cyanide or zinc cyanide form) versus cyanide destruction is made in Table 1, from which it is apparent that recycling could be economically attractive in many cases. In addition, the various unit operations needed for an ion-exchange cyanide recovery plant require relatively simple equipment, operated under ambient conditions. Note that the calculated cost of the recycled cyanide (between \$0.50 and \$0.95/kg NaCN recovered) is in the

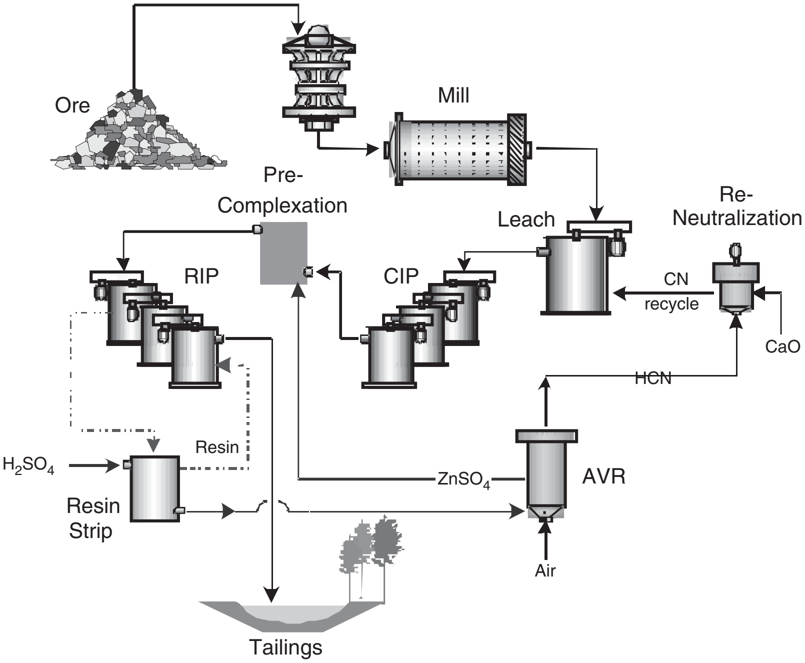

Fig. 4. Simplified flowsheet for cyanide recovery from gold tailings slurry by ion exchange with zinc pre-complexation.

Table 1
Operating cost comparison: Cyanide recycling by ion-exchange versus cyanide destruction

	Cost of recycled cyanide (per kg NaCN) ($/kg)
H_2SO_4 consumed at 1.5 kg H_2SO_4/kg NaCN (50% excess assumed)	0.15–0.30
Lime consumed at 0.9 kg/kg NaCN (20% excess assumed)	0.10–0.15
Resin and zinc losses, labour, power and maintenance (range based on size of plant)	0.25–0.50
Total	$0.50–0.95
	Cost of new cyanide (per kg NaCN)
Purchase price of new cyanide	1.00–1.50
Cost of cyanide destruction	0.65–2.40[a]
Total	$1.65–3.90

[a] The wide range of costs for the Inco process takes into consideration variable CN^- levels in the tailings (in the range 100–800 mg/L CN) and the variable cost of different SO_2 sources. Other CN destruction processes are more expensive than the Inco process.

same range as the cost reported by Botz and Mudder (1998) for a typical silver plant using the Cyanisorb Process (~$1.00/kg recovered NaCN), and that reported by Stevenson *et al.* (1998) for the Delamar Mine Cyanisorb plant ($0.80/kg NaCN).

The capital cost of the RIP plant (3 or 4 stages of extraction), plus the elution and small AVR plants, is likely to be in the US$5–10 million range, depending on the volumetric flow of tailings and the concentration of cyanide in the tailings. Based on the data in Table 1, the advantage of recycling over destruction will likely be $1–3/kg of NaCN in the tailings, which means that the time to pay back the incremental capital cost of the cyanide recovery plant will be relatively low (< 2 years) in most cases, and almost certainly less than the rest of the gold-plant.

Pros

- The process can be applied to solutions or slurries, circumventing the need for solid/liquid separation in the case of milling operations.
- Acid and lime consumption is stoichiometric because extraction (RIP) is conducted at the natural pH of the gold/silver plant tailings (pH 10–11).

- It is possible to recover all of the free and WAD cyanide in the gold-plant tailings without upsetting the water balance in the plant, and without the need for supplemental detoxification of the final tailings.
- Cyanide is pre-concentrated by ion exchange ahead of AVR, so it may be economically feasible to recover cyanide from lower grade feeds than would be the case with direct AVR on tailings. The economics of the Cyanisorb process indicate that cyanide recovery will produce more favourable economics than cyanide destruction in a 1000 tpd plant (or bigger) at CN concentrations of 100 mg/L or higher. A concentration of 200 mg/L will generate a fast payback (2 or 3 years) on the capital invested in a Cyanisorb plant (Mudder, 2004). While the economic break even for a plant that incorporates ion exchange by RIP ahead of AVR is not known at this stage, it could occur at even lower CN concentration.
- The AVR process is applied to a small, highly concentrated solution of HCN, and it is therefore potentially safer than direct AVR on tailings, and will be more efficient and rapid.

Cons

- No commercial installations have been built yet.
- The process is more complex than direct recovery from tailings (without preconcentration of the cyanide).
- Handling of concentrated HCN in a small AVR plant is potentially hazardous, and this part of the plant must be carefully designed and engineered.

The process should always be considered for the treatment of gold-plant tailings in which the recovered cyanide is present in the form of free cyanide or the zinc cyanide complex. Non-recoverable forms of cyanide (ferrocyanide and thiocyanate, for example) do not load as well as zinc cyanide on the resin, and can be rejected to the tailings if desired. If the tailings contain significant amounts of WAD cyanide in the form of the copper–cyanide complex, the zinc process is not ideal, and one of the processes described below should be considered.

4.4.2. Cyanide recovery by RIP extraction of copper cyanide

4.4.2.1. The AuGMENT process. The AuGMENT process was developed by SGS Lakefield Research and the DuPont Corporation (Fleming *et al.*, 1995) to recover copper and cyanide in gold-plant tailings, by an ion-exchange resin-based process. The chemistry involved in the various unit operations is based on the formation of different copper–cyanide complexes as the cyanide to copper ratio is varied, from $Cu(CN)_2^-$ at low CN/Cu ratio to $Cu(CN)_3^{2-}$ and $Cu(CN)_4^{3-}$ at high CN/Cu ratio. The tri-cyano species is the most stable form of the complex over a wide range of CN/Cu ratios. The ability to understand, measure, and control the CN/Cu ratio is one of the keys to successful operation of a plant using the AuGMENT process. The fact that copper cyanide does not break down completely during acidification, but rather forms the CuCN precipitate (Eq. (3)) is another key aspect of the AuGMENT Process.

During the loading cycle, the resin that is recycled from elution and regeneration back to the last stage of RIP loading contains a substantial quantity of precipitated CuCN within the pores of the resin. When this resin encounters the gold-plant tailings in the RIP plant, the CuCN precipitate in the resin reacts with the tri-cyano copper complex in the tailings, to form the di-cyano anionic complex, $Cu(CN)_2^-$. This species has a great affinity for strong-base resins, and because it has only a single negative charge, it can also load to high capacity on the resin, with each resin functional group loading one copper-cyanide anion:

$$(Ⓡ\text{-}NR_3^+)_2\,SO_4^{2-}\cdot CuCN + Cu(CN)_3^{2-} \rightarrow 2(Ⓡ\text{-}NR_3^+)\,Cu(CN)_2^- + SO_4^{2-} \tag{10a}$$

Once sufficient CuCN has been built up in the resin pores, the process is able to extract free cyanide efficiently, as well as the copper tri-cyanide complex, as shown in the following equation:

$$2(Ⓡ\text{-}NR_3^+)_2\,SO_4^{2-}\cdot CuCN + 2CN^- \rightarrow 2(Ⓡ\text{-}NR_3^+)_2\,Cu(CN)_2^- + SO_4^{2-} \tag{10b}$$

Once the resin is fully loaded with the di-cyano species (60–80 g/L Cu; 50–70 g/L CN), it is advanced to elution, where about half the copper on the resin is stripped by treatment of the resin with free cyanide or, preferably, a concentrated copper cyanide solution having a CN/Cu ratio of 4 or greater. This treatment converts the $Cu(CN)_2^-$ species on the resin into the *tri*-cyano copper complex $Cu(CN)_3^{2-}$, which can only occupy half as many resin functional groups, because of the double charge on the anion. Thus, half the copper on the resin is effectively eluted. This chemistry is shown in Eqs. (11a) (stripping with free CN) and (11b) (stripping with copper cyanide at a 4:1 CN/Cu ratio).

$$2(Ⓡ\text{-}NR_3^+)\,Cu(CN)_2^- + 2CN^- \rightarrow (Ⓡ\text{-}NR_3^+)_2\,Cu(CN)_3^{2-} + Cu(CN)_3^{2-} \tag{11a}$$

$$2(Ⓡ\text{-}NR_3^+)\,Cu(CN)_2^- + 2Cu(CN)_4^{3-} \rightarrow (Ⓡ\text{-}NR_3^+)_2\,Cu(CN)_3^{2-} + 3Cu(CN)_3^{2-} \tag{11b}$$

In both the above cases, the resin is left with the copper *tri*-cyanide species adsorbed on its functional groups, and the copper tri-cyanide species as the dominant species in the eluate solution. The final two steps in the AuGMENT process involve regeneration of the eluted resin and electrolysis of the eluate solution. The resin is treated with sulfuric acid during regeneration, converting the copper tri-cyanide complex into CuCN, which remains precipitated in the resin pores, and releasing 2 moles of HCN per mole of copper. The resin is now ready for recycling to RIP adsorption:

$$(\text{®- } NR_3^+)_2\ Cu(CN)_3^{2-} + H_2SO_4 \rightarrow (\text{®- } NR_3^+)_2\ SO_4^{2-} \cdot CuCN + 2HCN \tag{12}$$

Pilot-plant work at SGS Lakefield Research in the early 1990s showed that when the eluted resin and the sulfuric acid regenerant solution were contacted in counter-current flow, it was possible to achieve high concentrations of HCN (~50 g/L) and low residual acidity (pH 4–5) in the regenerant solution. The regenerant solution was then treated directly with alkali (lime or caustic), without the need to go through an AVR step, to convert the HCN into free cyanide for recycling to the leach. The regenerated resin contained 30–40 g/L copper at a CN/Cu ratio of ~1. Thus, the stoichiometry depicted in Eq. (12) can be achieved in practice.

The copper *tri*-cyanide complex produced in the elution step was treated by electrolysis in an open-tank rectangular cell, to plate out copper metal on stainless steel sheet cathodes and regenerate more cyanide. The anodes were pouched in Nafion membrane bags to prevent anodic oxidation of cyanide. Caustic soda was pumped to the anodes to neutralize the acid that was generated:

$$2Cu(CN)_3^{2-} + e \rightarrow Cu^\circ + Cu(CN)_4^2 + 2CN^- \tag{13}$$

The spent electrolyte is recycled to the elution part of the process, where the high CN/Cu ratio is needed to strip more copper off the resin. During the pilot-plant trials, a delta copper of ~20 g/L was maintained (60 g/L in the feed to electrolysis and 40 g/L in the spent electrolyte). Solution was bled from this circuit periodically to control the build up of CN, which is apparent from Eq. (13). The bleed stream was treated with acid to precipitate CuCN (which after filtration was recycled to the electrolyte feed) and HCN solution, which was neutralized with lime and recycled to leach.

The pilot-plant trials demonstrated that copper cyanide and free cyanide could be extracted from gold-plant tailings to low barren solution values (<10 ppm), in a continuous process that produced concentrated cyanide solution for recycling to leach (~100 g/L NaCN equivalent) and ~99.9% copper cathodes as products. Theoretical consumptions of acid and base are the same in this process as in the zinc complexation process described above; the AuGMENT pilot-plant work (Fleming, 2001) demonstrated that these consumptions were achievable in practice at ~10% excess. The economics of this process could be slightly more favourable versus cyanide destruction (because of the additional revenue from copper sales) than those depicted in Table 1, for the zinc cyanide process.

The AuGMENT marketing company has recently been dissolved, and the rights to this technology are held by the University of Reno in Nevada, USA.

Pros

- The same advantages as the zinc cyanide process, with the added benefit of revenues from the sale of cathode copper.

Cons

- No commercial installations have been built yet.
- The process is more complex than the zinc cyanide process. During piloting at Lakefield Research, it was shown that the CN/Cu ratio is a key parameter that must be closely monitored and, in some cases, controlled, through all the unit operations of loading, elution, regeneration and electrowinning. The requirement for continuous, on-line analysis of copper and cyanide in solution creates analytical challenges, and it is anticipated that the efficient operation of an AuGMENT process will require a highly skilled workforce.

4.4.2.2. The Hannah process. The Hannah process (patents pending) was also developed at SGS Lakefield Research, in collaboration with John A. Thorpe. Like the AuGMENT process, it was developed with the treatment of copper cyanide-bearing gold-plant tailings in mind, but is able to efficiently recover free cyanide and the cyanide associated with other WAD complexes as well. The process is based on extraction with anion-exchange resins, so it can also be applied to solution or slurry tailings.

While the details of the process cannot be published at this stage, since the application for patents is still under review, the following brief outline can be used to size major equipment and to calculate reagent consumptions:

- The process uses conventional, large-bead, strong-base resins.
- The main purpose of the process is to recover cyanide, but it can also recover copper, zinc and thiocyanate (as a concentrated solution or as a CuSCN precipitate). If desired, thiocyanate can be rejected by the process, and report to the tailings.
- The optimum cyanide removal efficiency will vary with pulp composition, environmental regulations and local costs, but will normally be >90%.
- Major reagent consumptions (principally sulfuric acid and lime) will

be very similar to the zinc cyanide process and the AuGMENT process, described above.
- Resin flow will be 0.6–1.2 L of resin per mole of cyanide recovered (cyanide equivalent loading on resin = 22–44 g/L).
- Resin phase retention times in the loading tanks will be 1–2 h. Two to four loading tanks in series will be typical.
- The volumetric ratio of tailings solution flow to countercurrent resin flow will vary with the composition of the tailings, but will typically range from 20:1 to 100:1.
- Total volumetric resin inventory in the plant (loading, elution and regeneration) is expected to be in the range of 0.5–2 times the volume of tailings solution processed per hour.
- Resin elution is done at ambient temperature, and the hold up time is about 1 h.
- Resin regeneration is preferably done in columns, in a residence time of ~2 h. The regenerant is alkalized to produce a concentrated $Ca(CN)_2$ solution for direct recycling to leach.

The Hannah process is expected to produce similar favourable economics as depicted in Table 1 above.

Pros

- The process enjoys the same advantages as the AuGMENT process, with the added advantage of being simpler to understand and operate.
- Unlike the zinc cyanide process, the Hannah process is able to treat tailings that contain both copper and zinc as WAD cyanide complexes, and produce separate precipitated zinc and copper by-products.

Cons

- No commercial installations have been built yet.

5. ENVIRONMENTAL, SOCIAL, HEALTH AND SAFETY BENEFITS OF CYANIDE RECYCLING

The discussion above has centered on the technical aspects of cyanide recovery and the economic benefits that could flow from the implementation of this technology. As shown, the favourable economics alone should persuade gold mining companies to seriously examine cyanide recovery versus cyanide destruction in their mills.

There is an even more compelling reason for gold-mining executives to seriously evaluate the option of recovering and recycling cyanide from gold plant tailings, and that is the positive impact that this technology will have on the environment and on the perception of the gold industry in the minds of the public, special interest groups, regulators and governments.

These less-tangible benefits of cyanide recovery can be summarized as follows:

- The current 'best' practice in the industry is to oxidize cyanide in gold-plant tailings to a WAD CN concentration of 50 mg/L or less, before release into a tailings dam, producing cyanate (and sometimes ammonia), and precipitating heavy metals plus strongly bound cyanide in the tailings. While this represents a significant improvement on the historical practice of releasing cyanide directly into tailings dams and allowing air and sunlight to slowly decompose the cyanide, cyanide detoxification cannot be considered a 'clean' technology. For example, salts such as sodium cyanate and thiocyanate accumulate in aqueous solutions (and ultimately transfer to the ground water) while heavy metals remain in the tailings. While those species are less toxic than cyanide, cyanate and thiocyanate represent a biological oxygen demand and nitrogen loading in aquifers, while ammonia is extremely toxic to aquatic life and is also a regulated substance.
- The lowering of cyanide entering tailings ponds by cyanide recovery, regardless of technique, has important advantages that go beyond the obvious environmental ones relating to protecting wildlife. Primarily, lowering the concentration of cyanide and its oxidation by-products produces seepage that is so much cleaner that long-term closure plans can be modified significantly to lower overall costs. For example, as a result of the installation of a cyanide recovery plant at the Golden Cross Mine in New Zealand, the seepage from the tailings pond was of sufficiently high quality that it could be discharged directly to the river, only 18 months after operations ceased at the plant. Furthermore, based on predictions of water quality at closure and dramatically reduced fears of groundwater contamination, it was possible to build the tailings impoundment without any liner (Mudder, 2004).
- The preferred reagent for transportation is solid sodium cyanide, which must be carefully handled during manufacture, shipping and unloading at the mine site, to avoid exposure of workers to toxic dust. Cyanide recycling reduces the need for new cyanide purchases, which in turn reduces cyanide handling and the risk of cyanide spills in transit to a mine site.
- Cyanide recovery technology will benefit local communities by extending the life of mines, by allowing mining companies to process lower-grade ores as well as ores that contain high cyanide-consuming minerals, such as copper sulfides and oxides. In several of the cyanide recovery processes,

copper is recovered and can generate extra revenue for the operator, instead of becoming the death knell of a mine, as is often the case today. The installation of cyanide recovery using the Cyanisorb technology at the DeLamar Mine in Idaho, USA, did indeed extend the life of that mine by several years.

6. CONCLUSIONS

Free and weak-acid dissociable cyanide are readily recoverable from gold and silver plant tailings solutions or pulps.

There are several processes available, and the choice of the best technology will be based on factors such as:

- The composition of the tailings, particularly relating to cyanide speciation in the solution phase.
- The form of the tailings (solution or pulp).
- The efficiency and cost of solid/liquid separation.
- The local environmental regulations for final discharge of tailings and bleed streams.
- The availability of local expertise and infrastructure.

In many cases, the cost of recycled cyanide will be less than the cost of new cyanide purchases, and capital investment to recover cyanide could be paid back in less than 2 years.

The implementation of this technology will reduce shipments and handling of new cyanide to mine metallurgical sites, reduce soluble salt loadings in tailings, and demonstrate proactive environmental stewardship to a public that has, in recent years, become increasingly hostile to mining in general and the use of cyanide in particular.

Cyanide recycle should be evaluated during project feasibility for all new gold operations, and should also be considered for retrofitting into many existing plants.

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Chapter 30

Tailings storage facilities

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1. EVOLUTION OF TAILINGS MANAGEMENT

The importance of sound tailings management as an industry issue is increasing dramatically. In their 2002 report to the World Business Council for Sustainable Development (*Breaking New Ground*), the Mining, Minerals and Sustainable Development Project highlighted the need for the mining industry to re-orientate its thinking with regard to waste management, particularly tailings disposal. In 2004 the Mining Association of Canada (MAC) announced a programme, *Towards Sustainable Mining*, designed to ensure that the actions and activities in the mining industry are aligned to the value of local communities, employees, stakeholders and the public at large. This programme initially focuses on Tailings Management.

Historically, tailings have received little serious attention in the industry, as shown by this quotation from the Tribunal into the Aberfan disaster (HMSO, 1967):

> *Rubbish tips are a necessary and inevitable adjunct to a coal mine, even as a dustbin is to a house, but it is plain that miners devote certainly no more attention to rubbish tips than householders do to dustbins.*

Very early records show that ore/gangue separation usually took place in or close to rivers, with the rejected gangue being allowed to contaminate the riverbed. In the late 19th and early 20th centuries, mechanization allowed considerably greater volumes of material to be mined and processed and the need to actively dispose of tailings arose. Many of those early, relatively small operations simply placed the tailings in

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some convenient depression near the process plant. As the volume of tailings increased, it became necessary to build engineered structures to contain the tailings. Hydraulic placement of tailings became a standard method of managing tailings, this method being particularly easy to integrate into gold operations where wet processing was the standard ore treatment method.

Over time, developments and improvements have been made in both the efficiency of ore processing and of material handling. This has led to a significant increase in the tonnes of ore milled, and hence volume of tailings produced per unit of gold recovered. This is evident from the statistics published by the Department of Industry and Resources, which show the dramatic increase in the tonnage of ore treated and the lowering of head grades for Western Australia between 1979 and 1995, as illustrated in Fig. 1.

The characteristics of gold industry tailings has also changed over time, with sand-sized particles being gradually replaced by slime-sized particles and more recent grinding developments leading to ultra-fine grinding, with a further reduction in average particle size. The phasing out of mercury as a gold recovery route has been an environmentally positive development, although the re-treatment of old mercury-rich tailings still poses a risk.

The failure of several tailings facilities in the last decade or so has resulted in many leading gold producers applying a rigorous risk management approach to the design and operation of their tailing systems. The risk-assessment process addresses environmental and social risks as well as the

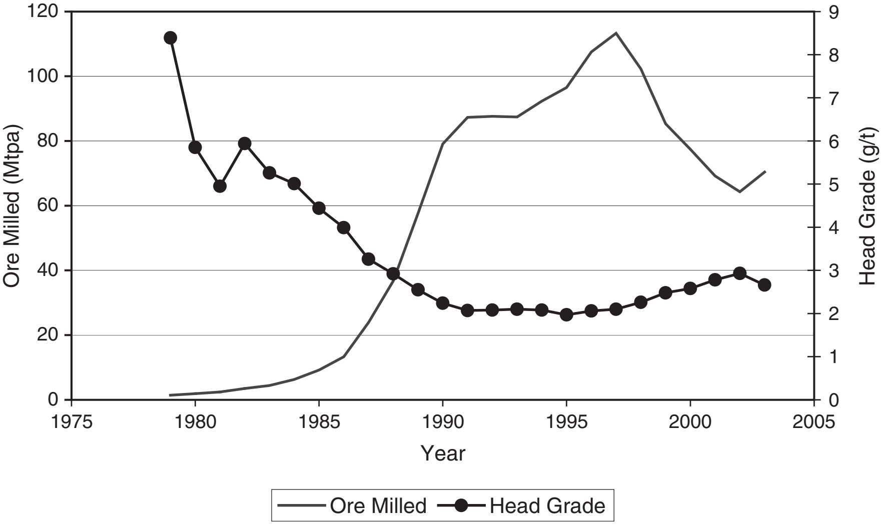

Fig. 1. Relationship between ore milled and head grade in Western Australia, (after Department of Minerals and Energy, 1996).

more common cost over-run and purely engineering risks, and tends to reflect current community trends.

2. PAST FAILURES

Failures of tailings storage facilities have been the subject of considerable negative publicity in recent years. The International Commission on Large Dams (ICOLD) summarized many of these events in a joint publication with United Nations Environment Programme (ICOLD, 2001). The publication (Bulletin 121) does not specifically identify gold operations, but (as many of the techniques of TSF construction and management are not significantly different to the rest of the mining industry) the general observations in the Bulletin may be considered to apply. The Bulletin concludes the following:

> *Causes in many cases could be attributed to lack of attention to detail. The slow construction of tailings dams can span many staff changes, and sometimes changes of ownership. Original design heights are often exceeded and the properties of the tailings change. Lack of water balance can lead to "overtopping": so called because that is observed, but may be due to rising phreatic levels causing local failures that produce crest settlements.*
>
> *Causes include problems of foundations with insufficient investigations, inadequate or failed decants, slope instability, erosion control, structural inadequacies and additional loading of closed impoundments. Most situations have already been solved by engineering technology, indicating that a more systematic application of the specialized knowledge is required.*

The minimization of the risk of tailings storage facility (TSF) failure may be achieved through the establishment of a best-practice tailings management plan.

3. CONSTRAINTS AND DRIVERS

As mining advances into the 21st century, the following factors are significantly influencing what is considered to be the appropriate best practice in tailings management in the gold industry.

3.1. Public perceptions and politics

The mining industry generally suffers from a low public image because the majority of the public do not relate the items they need and use on a day-to-day basis with the industry. The very large-scale earthmoving activities of the industry are often considered to be environmentally damaging while the well-rehabilitated former mine sites are often not recognized for being just that. Add to this the fact that a major reagent consumed by the gold industry is cyanide and the public perception of the tailings produced by the industry becomes very negative.

Each 'incident' associated with gold industry tailings therefore produces a negative public reaction, which can under some circumstances result in public outrage, political pressure and finally restrictive legislation or even industry prohibition.

3.2. Legislation

Legislation is generally enacted *after* an unacceptable event has happened. Moreover, legislation normally becomes more technically prescriptive as a community's perception of risk increases. From a legislative perspective, tailings operations can be regulated as four separate but inter-related phases, namely:

- Approval
- Construction
- Operation
- Completion (or closure).

Regulation of tailings systems in most jurisdictions in the world is normally the responsibility of more than one government department or instrumentality. Commonly mentioned departments are Mines, Environmental Protection, Public Works, Water, Natural Resources and Employee Safety. Any or all of these government departments can be seen to have a legitimate role in regulating tailings systems in the mining industry. In some cases there is more than one level of government (e.g., national and local), which can sometimes have very different goals regarding individual operations.

Where jurisdictions have well funded and technically developed regulators, employing geotechnical engineers experienced in tailings management and experienced environmental experts, the regulations are not prescriptive. Each facility can be assessed on a case-by-case basis and the 'one-size-fits-all' technical prescription is not needed. With the increasing international awareness of the risk potential of tailings (mis)management there has been the publication of a number of guidelines and codes of practice, by governments and non-government organizations, which should result in these codes and standards relating to tailings becoming 'harmonized' internationally.

4. TAILINGS CHARACTERIZATION

Understanding of the physical and geochemical properties of the tailings and associated transport liquor generated through mineral-processing operations is fundamental to the development of a 'best practice' tailings management plan. Characterization of the tailings and the transport liquor involves carefully considered laboratory and field testwork programmes to measure the relevant properties and performance of the materials. The successful design, implementation and performance of the tailings management plan will rely on the appropriate identification and understanding of these properties.

It is likely that key design components of the TSF will depend heavily upon specific tailings properties. For example, potential for long-term acid generation of the material, tailings permeability and consolidation characteristics as well as the cyanide content of the tailings slurry may influence embankment and underdrainage design, as well as the requirements and specifications for liners and covers.

4.1. Physical characterization

The physical characteristics of gold tailings that need to be measured or estimated from field and laboratory testing may include many or all of the following:

4.1.1. Particle size distribution

It is important to measure the particle size distribution (PSD) of the tailings down to at least single micron (1 μm)-size fraction, thus covering the clay, silt and sand size fractions. Normal sieve analysis will only allow for size measurements down to 75 μm, thus necessitating an alternative means of measuring particle sizing below this size fraction. Measurements of particle sizes finer than 75 μm may be achieved through hydrometer analysis, laser sizing or the X-ray scanning (*Sedigraph*) method (while conventional screen sizes down to 38 μm are available, physical screening can become time-consuming at these sizes). Each of these has its own potential benefits and pitfalls, and a specialist geotechnician should therefore be consulted before selecting a particular method. For example, it may be inadvisable to select the hydrometer method if the tailings transport water is hypersaline.

It is also prudent to carry out a particle (solids) density determination when measuring the tailings PSD.

The outcome of the particle size distribution and solids-density measurements will provide preliminary key information to the design engineer on the likely engineering performance of the tailings. There are numerous empirical relationships that can be used to provide estimates of other key properties from a PSD. These include estimation of shear strength; *in situ* porosity (and hence dry density/TSF volume requirements); sedimentation; beaching; consolidation and permeability behaviour, all of which should be supported later by dedicated testing and measurements.

4.1.2. Atterberg limits

The *Atterberg limits* (*liquid limit*, *plastic limit* and *shrinkage limit*) provide a very useful indication of the properties of the tailings. They have been used in soil mechanics for over 50 years, providing a measure of the moisture content at which a soil (tailings) changes from a liquid to a plastic, a semi-solid, or a solid state (moisture content is defined as the mass of water divided by the mass of dry solids). In particular, the arithmetic difference between the liquid limit and the plastic limit (the *plasticity index*) is a particularly useful indicator of probable soil properties.

To provide an empirical reference of probable physical performance, therefore, it is advisable and common practise to at least determine the liquid limit and the plastic limit of the tailings.

4.1.3. Settling and drying properties

The rate at which tailings solids settle out of suspension in the transport liquor is a fundamental property of the material that impacts upon a number of *in situ* features of the deposited material. These include the initial dry density, amount of retained (and hence released) liquor and beach slope angle and shape (linearity). These features of the deposited tailings need to be taken into account in the design of the storage facility.

Air-drying of the tailings may be carried out in the field or in the laboratory. The moisture content of the exposed tailings is measured from samples extracted from the exposed area at appropriate time intervals. It is preferable to carry out the test under controlled temperature and humidity conditions. These can be varied to mimic seasonal climate differences. Wind effects can also be simulated if necessary.

The moisture content of the tailings is plotted against time, with a view to establishing the long-term equilibrium moisture content and the time to achieve this. The rate of increase, and the ultimate exposed *in situ* dry density of the deposited tailings can then be estimated. The design rate of rise of the tailings beaches needs to take cognizance of these parameters.

4.1.4. Permeability

The permeability of the deposited tailings plays an important role in the rate at which consolidation occurs, the allowable rate of rise to maintain stability, the rate and amount of seepage emanating from the TSF. Tailings permeability therefore impacts significantly on a number of key design factors and features.

Tailings permeability is primarily controlled by the particle size distribution of the tailings solids (and can be approximated from the PSD). Other factors that influence permeability include the porosity and density of the material (which are, in turn, influenced by the degree of consolidation), the mineralogy of the tailings solids and the chemistry of the pore liquor.

Permeability properties can be measured in the laboratory by either falling-head or constant-head permeameter tests. This *permeameter* is essentially a clear cylinder containing saturated tailings, that has drains at both ends and is fed from a reservoir of liquor (usually tap water). The volume of water passing through the tailings is measured (together with differential head measurements) and the data used to calculate the vertical coefficient of permeability (K_v) of the tailings. For gold tailings, this value is commonly between 10^{-7} and $10^{-9}\,\mathrm{m\,s^{-1}}$. K_v can also be back-calculated from the results of consolidation testing in the oedometer (see below), or measured directly as a component of more sophisticated consolidation testing (e.g., Rowe Cell tests, triaxial testing and centrifuge testing).

It is important to note that the horizontal coefficient of permeability (K_h) is much more difficult to measure, and is usually estimated according to a judged *anisotropy* (ratio of K_h:K_v) of the deposited tailings. The anisotropy will vary from tailings to tailings and from condition to condition, but it is an important parameter for use in seepage analyses and hence may impact significantly on the TSF design. Common practice involves conducting sensitivity analyses on the various design studies to a range of anisotropies, typically (for subaerially deposited gold tailings) from 2 to 10. Thus, if the measured $K_v = 5 \times 10^{-7}\,\mathrm{m\,s^{-1}}$, then $K_h \approx 10^{-6}$ to $5 \times 10^{-6}\,\mathrm{m\,s^{-1}}$.

4.1.5. *Consolidation behaviour*

The key factor influencing the consolidation behaviour is permeability, which is, in turn, most heavily influenced by the particle-size distribution. Generally, the finer a tailings is milled, the longer it will take to consolidate. Other factors, however, such as mineralogy and the particle packing and shape will have an influence on the consolidation behaviour, and a direct relationship between PSD and the time to consolidate cannot be reliably inferred.

Measurement of consolidation coefficients (for use in consolidation and settlement calculations) is most simply and commonly carried out in an oedometer. More sophisticated equipment and methods can be employed where appropriate (e.g., for measurements at very low density, or up to very high stresses, or where more direct means of permeability estimates are required). These include triaxial and centrifuge testing, as well as the use of more advanced adaptations of the oedometer, such as the Rowe Cell.

4.1.6. *Shear strength*

The shear strength of the deposited tailings is of paramount importance in the design of the TSF. The stability of the facility will be related to many factors, including the geometry of the facility, the location and amount of water in the tailings and the fundamental drained and undrained shear strength of the tailings.

The measurement of the shear strength of the material is usually carried out in the laboratory using either a *shear box* or a *triaxial* apparatus. The parameters obtained from these tests are utilized in limit equilibrium stability analyses, the results of which are necessary to demonstrate the inherent stability of the TSF.

4.1.7. Beach evaporation

The measurement of evaporation from the beach of the TSF may be important when considering the TSF water balance. Measurements are made through the use of *micro-lysimeters*, which comprise two neatly fitting cylindrical containers, manufactured from uPVC. The instrument is snugly embedded in the tailings beach and the inner of the two containers is filled with tailings extracted from the beach. By removing the inner container, weighing it and replacing it on a regular basis, the loss of water can be measured. The outer cylinder of the micro-lysimeter holds the sample position open while the inner container is being weighed. Measurements can be cross-checked with atmospheric conditions (sunlight, pan evaporation, temperature, humidity, etc.) and relationships developed for the evaporative loss of moisture from the tailings.

4.1.8. Rheology

Thickening of gold tailings prior to disposal is typical and in recent years it has become more common to thicken the tailings to a *paste* consistency, either for backfill purposes, or to minimize water losses and environmental impacts. Gold tailings therefore usually exhibit non-Newtonian behaviour and the understanding of rheological properties is particularly important in slurry pump and pipeline design.

Rheological studies should be carried out to establish material properties for optimizing pump and pipeline design, the desirable slurry concentration from a deposition/drying viewpoint and the dewatering properties of the tailings.

4.1.9. Piezocone investigations

The *piezocone* is a device that is used with increasing frequency to investigate and facilitate characterization of *in situ* properties of deposited tailings. The device is pushed vertically into the tailings beach with a suitable jacking arrangement and measurements of penetration resistance and pore pressure are taken. The design of the test programme requires careful consideration and the results should be interpreted by an appropriately qualified and experienced geotechnical specialist. Nevertheless, the information can be used through a number of empirical relationships to provide reasonable estimates of *in situ* pore pressures, shear strength, permeability and coefficient of consolidation.

4.2. Geochemical characterization

Many gold operations process ore that contains sulfide minerals, which have the potential to oxidize over time and generate acid. This process can, in turn, lead to the concentration and mobilization of heavy metals, which may be present in very low concentrations in the tailings, leading to contamination of the local groundwater.

Assessing both the acid-generation and the acid-neutralization potential of tailings prior to placing them in the tailings storage facility is the first stage in developing an effective acid-management plan.

Both acid-generation and acid-neutralization tests are normally initially conducted in a laboratory on small samples so that the net acid-producing potential (NAPP) can be estimated. In most mines the ore will vary over the life of the operation and truly representative samples of ALL ore types should be investigated for their acid generation and neutralization potential.

4.2.1. Static testing

Static tests are conducted at one point in time and are indicative of the acid-generating potential. Care needs to be exercised though as many acid-generating minerals have a faster reaction time than the acid-neutralizing minerals. Acid-base accounting (ABA) usually involves a paste and rinse pH procedure, where the pulverized rock is mixed with distilled water and the pH determined. Acid potential may also be estimated through the use of sulfur analysis, with total sulfur being expressed as %S. The resulting value is often referred to as the maximum potential acidity (MPA). Another common static test measures the acid-neutralizing capacity (ANC) of the tailings, although this is often affected by the variable reaction rates of the acid-neutralizing minerals.

The net acid generation (NAG) test is a preliminary screening technique commonly used to reduce uncertainty associated with NAPP estimates based on ANC and MPA values. ($\text{NAPP} = \text{MPA} - \text{ANC}$). The NAG test can be static, with the results only being collected at the end of the test period or kinetic, with results being collected at intervals.

4.2.2. Kinetic testing

Kinetic testing is conducted either in the laboratory or in the field. These tests are designed to determine the relative rates of acid generation and neutralization, which determine the geochemical conditions, including whether a sample will acidify, the time to acid generation onset, and the drainage chemistry and the resulting downstream loadings for the predicted geochemical conditions.

A number of models exist to assist in the prediction of NAG potential at an operation. Considerable detailed information is required by most models, including determination of sulfide species, grain-size analysis, detailed mineralogy of all materials in the tailings, particle surface-area information, process liquor chemistry and local environmental data.

5. RISK-BASED DESIGN

The development of an appropriate tailings management plan requires the identification of *hazards* (factors that can potentially cause harm) and *risks* (likelihood of occurrence × consequences thereof) relating to the operation. Modern practice requires that each tailings management plan be developed site-specifically, taking cognizance of the specific risks relating to the operation. It is generally no longer considered acceptable to merely mimic an approach that has been used elsewhere, or in the past at the same site, without considering the hazards and risks relating to the future operation.

The risks relating to a tailings management plan fall broadly into the categories of *engineering* risk, *environmental* risk and *economic* risk. Appropriate strategies are required to address all identified risks in each category. This may be achieved through a systematic approach that broadly embraces accepted risk-management techniques as follows:

- *identification* of hazards;
- *preparation* of preliminary design concepts;
- *assessment* of risks associated with concepts;
- *modification* of design to address high-risk areas;
- *re-evaluation* of risks, including development of a risk management plan;
- *finalization* of design;
- *implementation*, and
- *ongoing* monitoring, design improvements and risk management.

In the development of the design concepts, it is important to consider the impacts that the tailings management plan may have on aspects of the mining operation outside of the TSF. Modern practice, for example, requires that there is an integration of water-management issues relating to tailings management with water management elsewhere on the mine.

Tailings are frequently a major user of water and the consideration of methods to minimize the loss of water may assist in simultaneously minimizing the engineering, environmental and economic risks. In recent years, it has therefore proved beneficial to concurrently consider plant process options with tailings management options, potentially reducing water consumption as well as overall reagent costs.

The development of an appropriately designed and managed TSF requires consideration of a multitude of frequently inter-related and potentially conflicting factors that may impact on the selection of an appropriate design. Some of these are listed below and may best be collectively considered in context through a risk-based design approach as discussed above.

(1) **The general location**

- *environmental sensitivity* (for example, rare or endangered species, proximity to unspoilt areas or national parkland, water supply area);
- *climate* (for example, high rainfall, sub-zero temperatures);
- general *topography* (for example, very steep, proximity to water courses);
- regional *geology* (for example, possibility of karsts, collapsing or dispersive soils, shear zones, existing or potential undermining, shortage of construction materials, high water table), and
- *seismic hazard* (high earthquake loading).

(2) **The material**

- *geochemical* character of tailings (for example, potentially acid forming, high pH liquor, heavy metals, noxious reagents), and
- *physical* character of tailings (for example, low strength, poor consolidation or drainage properties).

(3) **The site**

- downstream *infrastructure* (what are the consequences of a release of tailings or liquor, however remote this may be perceived?);
- *proximity* to the process plant (is it as close as possible to minimize transport costs?);
- tenement/cadastral *boundaries* (is it constrained so that it is too small, of an awkward shape or restricts potential future expansion?);
- potential underlying *mineralization* (is there a possibility of future undermining?);
- *topography* (is there a possibility of surface water erosion or flooding?), and
- *geology/hydrogeology* (do the geotechnical properties mean that special design measures are required?).

(4) **Management**

- tailings *deposition method* (is the proposed method the most appropriate for the conditions?);
- *water balance* (is there a potential shortage/surplus of suitable water?), and
- *monitoring* (are special methods required?).

(5) **Other environmental considerations**

- *socio-economic* factors (for example, does the facility provide community employment, or impact detrimentally on quality of life through dust or aesthetics?).

After consideration of the above factors and the adoption of a risk-based design, the risks can potentially be further reduced by conducting a peer review of the design proposals.

6. RECENT MAJOR ADVANCES

Many of the recent advances in tailings technology have been driven by the need to meet community expectations, conserve water and reduce overall costs.

Tailings can be managed in a number of forms, broadly classified as conventional (unthickened) slurry (typically for gold tailings less than ~45% solids), thickened slurry (~45–55% solids), paste (~70–75% solids) and filter cake ($>$75% solids). These forms are essentially four stages of progressive dewatering. The main differences between the forms are:

- the locations where the final separation of the solid and liquid takes place;
- the time period this happens over;
- the de-watering technology involved, and
- the degree of control the operator has over the recovered water.

Table 1 indicates a qualitative comparison of the various 'properties' of the four main tailings management options.

Capital and operating costs are major contributors to any decision made on the tailings-management plan for an operation. Historically, the low capital and direct operating costs have been the major drivers in the selection of the tailings system. The often very considerable cost of completion (closure) was not normally taken into account, in part because little hard historical data on this aspect of operations was available.

Table 1
Qualitative Comparison of Tailings Properties

	Slurry	Thickened slurry	Paste	Filter cake
Segregation	High	Slight	None	None
Supernatant water	Considerable	Some/Slight	None	None
Post-placement shrinkage	Potentially significant	Some/Slight	Insignificant	Negligible
Seepage	High	Some/Slight	Insignificant	None
Availability for rehabilitation	Delayed, often considerably	Almost immediately	Almost immediately	Immediate
Potential placement	Above ground or open pit	Above ground or open pit	Above ground, underground or open pit	Above ground or open pit
Angle of repose on beach	Up to 1°	1–3°	3–10°	Up to erosion angle of material (~14°)
Potential water recovery	Up to 53%	Up to 67%	Up to 82%	Usually over 80%
Reagent recovery	Lowest	Medium/High	High	Highest

Currently, more and more companies require consideration of the long-term environmental and social aspects as well as the short financial aspects of decisions they make, which requires the total cost, including the completion (closure) costs to be included in any cost estimate of tailings management. Initial data indicate that conventional slurry TSFs are significantly more costly to rehabilitate than an equal surface area of dry tailings, with some operators suggesting a multiplier of 5 or more.

As more and more companies adopt *triple-bottom-line* principles and a *whole-of-mine-life* approach to mining developments, the selection of tailings management systems is required to address many more issues than simple operating and capital costs. Thickened tailings, paste and filter cake may have been considered ‘over the top’ as methods of surface tailings disposal in previous decades, but for future mining operations they could become the only acceptable methods.

6.1. Water reduction

There are two main drivers for reducing the amount of water placed on tailings storage facilities:

- the *scarcity* (or cost) of water, and
- the *risk* posed by water in a system malfunction.

For example, scarcity of water (coupled with a plan to utilize underground backfill) at the Bulyanhulu mine in Tanzania has resulted in the adoption of a water-reducing (paste) surface tailings management system. Moreover, the prospect of increasing water costs in South Africa has seen a number of operators revise their operating practices, moving towards higher-density slurries.

Two major tailings ‘events’, the Omai leakage in Guyana and the Baia Mare overtopping in Romania (see also Chapter 8) highlighted the potential environmental impact of the gold industry’s cyanide-rich tailings liquor, and a third event, the Merriespruit failure in South Africa, showed the destructive potential of water held on tailings storages. These events would most probably not have taken place if standing water had not existed on the tailings-storage structures.

A number of companies are considering going to the extreme stage by removing process water from their tailings by using filter systems to produce a dry filter cake that is then disposed of at the surface. Both disc and belt filters have been considered for these applications, with environmental risks being the major factor in considering such options.

6.2. ‘Dry’ tailings

The use of large-capacity vacuum or pressure-belt filters offers the chance to dispose of tailings in a ‘dry’ condition, with the resulted benefits of small footprint, no embankment requirement, ease of closure and lower potential environmental impact. However, these systems have the highest operating cost and can be prohibitively expensive for many applications. Nevertheless, they have been adopted in arid areas, where water conservation is a major concern and in very cold areas where water handling out of doors is a major problem in winter.

6.3. Centrally thickened discharge

The placement of thickened tailings normally seeks to develop a cone-shaped landform, with the tailings being discharged at a central location and allowed to flow away from the discharge point. This technique, often called centrally thickened discharge (CTD), relies on the tailings being relatively consistent in water content and essentially non-segregating. As the angle of repose of the tailings is shallow, relative to paste, the system requires extensive areas for deposition if limiting embankments are not used. The system has been most successful in more arid locations.

6.4. Backfill

Backfill operations have been used for effective and safe underground mining for many years. The normal technique has been to take a selected portion of the tailings stream for backfill (usually the sand fraction), with the balance (usually the slimes fraction) being disposed of in the tailings storage facility. A significant operational difficulty with this method has been the need to manage the substantial volume of water used to transport the tailings to the required area.

The development of paste technology in recent years has considerably reduced these operational difficulties and made tailings placement a much more acceptable mining practice than had previously been the case. Commonly, the total tailings product can now be placed underground as an acceptable paste backfill (frequently strengthened and stabilized through the addition of cement). This has enabled the placing of environmentally 'difficult' tailings underground, as is the case at Henty in Tasmania, where potentially acid-generating tailings and other waste rock are backfilled as paste.

6.5. In-pit storage

The development of many open-pit gold mines has resulted in the availability of worked-out open pits in close proximity to gold-processing plants. A number of operations have successfully utilized these pits as tailings-storage facilities. The open pits used for this method of tailings management have included pits where all storage is above the local groundwater, as well as pits where the majority of storage has been below the groundwater table. The potential for the deposited tailings to dry out and form a safe, final land surface is an important design consideration in this type of TSF, with some publications indicating that this drying out could extend over several decades.

The design of an appropriate in-pit system therefore requires careful consideration of the consolidation behaviour of the tailings (and consequential long-term settlements), the need (or otherwise) for an underdrainage system, other measures to protect the adjacent groundwater system and methods of short-and long-term water extraction.

There are a number of advantages in this form of disposal including the elimination of embankment failure, the utilization of otherwise unusable land and considerably reduced long-term erosion potential.

6.6. Lining of tailings storage facilities

Cyanide used in most gold processing is normally an unstable compound that breaks down naturally on exposure to air and ultraviolet light. It can, however, be more stable in groundwater and migrate long distances as a result. For protection of aquifers it is sometimes necessary to place an engineered liner across the base of the tailings impoundment.

Liners may be as simple as the selective placement of impervious soil or may comprise a composite liner system, formed from synthetic *geomembranes* and natural soils. Where geomembrane liners are used it is normal practice to incorporate a drainage layer above the geomembrane to facilitate dissipation of pore pressures in the deposited tailings.

An underdrainage system will typically comprise a 300-mm-thick layer of granular material, with perforated pipes at regular intervals within the drainage layer. The pipes are laid to drain the water extracted from the tailings and discharge it to a seepage recovery pond.

The success of a liner is critically dependent on the care taken during its installation as any damage to the liner will very seriously impair its long-term performance.

6.7. Management of acid mine drainage

One of the most significant challenges to managing tailings is the increasing use of sulfide minerals for ore feed and, therefore, the increasing amount of sulfide minerals being placed in the tailings-storage facilities. Here, the sulfides will almost certainly oxidize over time and this may result in the production of sulfuric acid, a process commonly called acid mine drainage (AMD).

A number of strategies that can be adopted to minimize and manage the generation of acid, include the use of selective flotation so that the sulfide minerals can be concentrated at designated locations and managed effectively. Dissemination of sulfide-bearing minerals throughout a tailings-storage facility means that any acid generated is essentially unmanageable and poses a high risk of long-term chemical pollution.

When potentially acid-generating sulfide minerals are placed above the water table there are three broad approaches to minimizing the adverse impacts of AMD, as follows:

- *minimization of oxygen contact* with the sulfides to prevent oxidation;
- *containment of acid* generated at the acid-production location, and
- *treatment or neutralization* of acid produced before it can be released into the environment.

Two methods are generally advocated for sealing off potentially acid-generating sulfides with an impervious barrier, one normally used in more arid areas and the other in higher rainfall regions. Both techniques are intended to have a two-fold effect, by reducing the rate of oxygen ingress, as well as minimizing the flow of water through the structure and therefore the transportation of any sulfuric acid generated.

In arid areas, the seal or capping often uses impervious clays, sometimes multi-layered, which may or may not have a vegetation supporting soil layer on top. The cap is normally designed to shed almost all of the incident rainfall. A variation of this is the *stores and release* cap, designed to accommodate the incident rainfall, where that rainfall is seasonal, with subsequent release through evaporation and the evapo-transpiration action of the vegetation established on the structure.

These techniques have potential problems due to the cracking (and therefore failure) of the cover materials during seasonal weather conditions and changing climate, as well as the penetration of the sealing layer by naturally establishing vegetation.

The sealing technique more often employed in wetter regions utilizes a water barrier or cover as an effective way of inhibiting the ingress of oxygen into the tailings pile. However, the long-term risks posed by having water stored on top of a tailings-storage facility are frequently considered to be unacceptably high. This technique of flooding the structure at the end of its operational life is therefore less popular because it exchanges one set of risks for another, rather than eliminating or reducing total risk.

The placing of tailings into an existing lake or the ocean is a more effective way of reducing acid generation in the long term, but brings with it other environmental consequences, which may also be unacceptable.

Placing potentially acid-generating tailings back underground as backfill or into worked-out open pits below the natural water table are much more reliable methods of managing potentially acid-generating tailings.

7. TSF COMPLETION OR CLOSURE

The mining industry frequently puts forward the position that it is a temporary user of land. Adopting this position requires that the industry return the maximum amount of land to a sustainable and constructive post-mining use. While all mining operations are finite, the tailings-storage facilities constructed during these operations will be expected to remain in place for an almost infinite period of time after cessation of operations.

The closure design of any TSF therefore needs to address the long-term stability, safety and aesthetic aspects of the structure while assessing the potential post-operational land uses of the TSF. These matters require close consultation with the stakeholders (including government authorities and the local communities) so that the final closure design will meet the reasonable expectations of those stakeholders at a cost acceptable to the operating company. While this topic is addressed in more detail in Chapter 11, planning for closure is worth consideration from the design phase of a project.

7.1. Safety

The term *safety*, when applied to a decommissioned TSF by governments usually means *public safety*, including the possibility of a post-operational breach of the TSF embankment, the possibility of the public gaining access to the structure and falling down steep slopes, being trapped (or worse) in any remnant decant pond and children being accidentally buried in the easily excavated material. Another concern is that liquor seeping from the TSF will have a harmful effect on groundwater, particularly when cyanide has been placed in the TSF during operations. A further concern is the potential for the contained tailings to generate acid and leach heavy metals into the groundwater systems.

A common complaint made by members of the public to regulators concerns the amount of dust generated by abandoned TSFs in dry climates. While not strictly a safety issue, regulators often treat it as a public health matter.

7.2. Stability

Two types of stability problems can affect TSFs after closure (particularly above-ground facilities, involving a high containing embankment):

- acute *slumping* of the external sides of the embankments, and
- chronic *erosion* of these embankments over a considerable period of time.

While the acute slumping affects very few TSFs, all are influenced to some degree by chronic erosion of the embankments. Generally speaking, wind erosion is the greatest problem in arid areas and water erosion in wetter areas.

The rates of erosion can be very high, with Blight and Amponsah-Da Costa (1999) reporting rates of up to 1,000 tonnes per hectare per year for unprotected slopes in gold tailings in South Africa. These rates can be significantly reduced through the establishment of vegetation covers, but they still remain quite high, with Blight reporting up to 200 t/ha/y for vegetated slopes from his South African studies (Fig. 2).

Three factors that have a major effect on the rate of erosion of any slope, are slope length, the slope angle and the surface shear strength of the slope.

There are, however, few examples of civil engineering structures capable of performing satisfactorily for 100 years without maintenance or replacement. It follows that attaining long-term stability will need to rely more on geomorphological considerations than on conventional ‘hard engineering’ solutions, with a minimum of straight lines and flat surfaces.

7.3. Aesthetic acceptability

Aesthetics is difficult to define, as every individual has his or her own definition of the word. However, most people would like the TSF to blend in with the surrounding landscape. Most natural slopes that are not rock

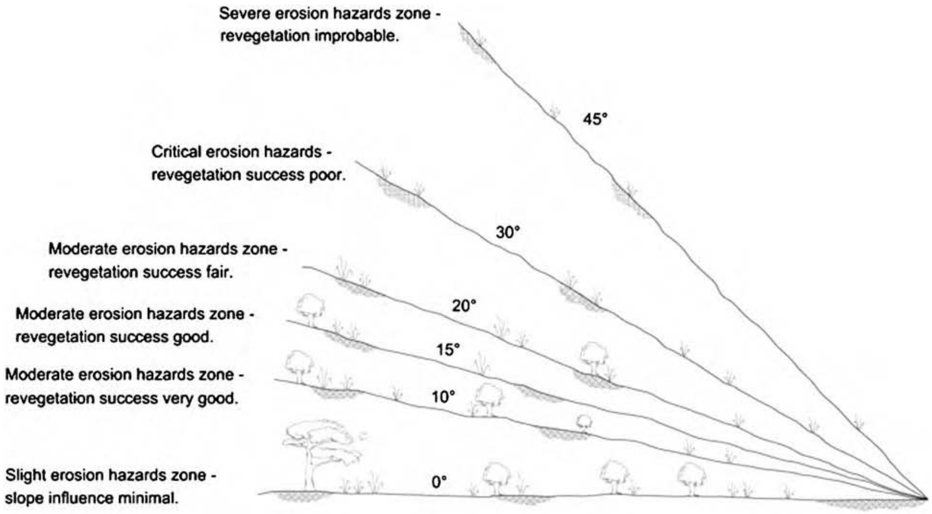

Fig. 2. Relationship between slope, erosion potential and revegetation (after WA Department of Industry and Resources, 1996).

outcrops have an S-shaped cross-section, with hills shedding the majority of incident rainfall (Fig. 3).

Mine closure landforms that are generally accepted aesthetically are those that are consistent with the regional context; that is, they should be not dissimilar, in shape and in scale, to the naturally occurring landforms of the region. While this objective is predominantly driven by landscape values, it can also be viewed as potentially improving landform sustainability.

Establishing vegetation on the TSF should be undertaken as soon as practicable. The outer slopes of TSFs can have vegetation established on them progressively, but vegetation cannot be established on the upper surface of the TSF until after deposition ceases.

8. FUTURE POSSIBILITIES

The future of acceptable tailings management may lie in one or more of the possibilities discussed briefly below.

8.1. Paste

Paste is a non-segregating material, both when placed on a tailings beach and when reticulated in a pipe. Producing tailings as a paste for disposal potentially offers a number of advantages over using conventional tailings,

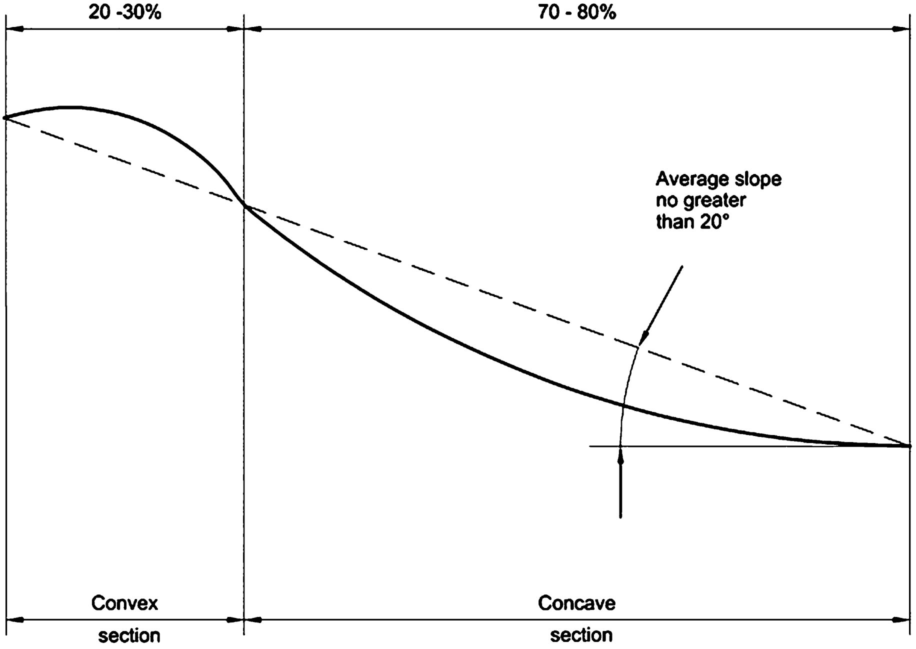

Fig. 3. Elements of a 'natural' slope (after WA Department of Industry and Resources, 1996).

which include the following:

- The higher density and lack of excess water indicate that paste is placed considerably closer to its final density, with very little post-placement settlement or consolidation. This allows for *access to the surface* of the material shortly after placement. This is a major advantage as rehabilitation can occur soon after placement, thus limiting potential erosion.
- The lack of excess bleed water in the paste means that *seepage is minimized*, thus significantly reducing potential contamination of local groundwater. This may make the use of cyanide more environmentally acceptable.
- Paste can be placed at relatively high angles of between 3 and 8°, while conventional tailings beach at flatter angles, typically less than 1°. This coupled with the lack of water significantly *reduces the land required* for paste disposal.
- Paste has less free or supernatant water than slurry tailings, thus *lowering the liquefaction potential* in the event of seismic activity.

8.2. Co-disposal of mine wastes

The co-disposal of thickened tailings or paste with coarse mining wastes provides the potential to form a homogeneous mass of material possessing improved engineering parameters and behaviour. This is achieved through filling the void space in the waste rock and making better use of the available storage volume, which in turn:

- reduces the permeability of the waste rock;
- improves the stability of the tailings, and
- removes the need for a tailings 'dam'.

Identified methods for achieving co-disposal are:

- autogenous mixing over an angle of repose face;
- active mixing at the crest and pushing over the face by dozer;
- windrowing of waste rock with the tailings placed in between and waste rock progressively dozed over the top, and
- constructing cells of waste rock into which tailings are placed.

8.3. Geotubes

Geotextiles have been used in geotechnical engineering since the 1960s in separation, filtration and reinforcement applications, and their use is now commonplace. One particular use of geotextiles is in the area of dewatering silts and sludges, including municipal and agricultural sewage sludges, industrial sludges and mine slurry or paste tailings. In this regard, geotextiles may be very cost-effective compared to mechanical dewatering.

At modest production rates, the use of geotextiles for tailings dewatering and storage may also be cost-effective and have other benefits when compared to conventional tailings storage options (e.g., erosion resistance, reduced potential for release through liquefaction, and ease of rehabilitation). Permanent dewatering of slurries and pastes can be effected with on-site storage of the final dewatered product in long geotextile tubes with an elliptical cross-section. Tubes used for dewatering can be up to 100 m in length, with effective volumes of 500–5,000 m^3.

High-strength woven fabrics are sewn into geotextile tubes that can be easily transported to site and filled with a sludge pump. The effect of surface tension and containment due to the tube geometry provide efficient dewatering characteristics. Once contained and dewatered, the material can be used as fill, often as part of a structure, or fitted into the landscape as part of mine closure works.

8.4. High-sulfur management

Practical management of tailings with a high concentration of sulfide minerals may require the separation of these minerals from the main tailings stream and their storage in a separate, specially designed facility. This will require a separation process, such as gravity or floatation after gold extraction, but will allow the bulk of the tailings stream to be placed in a normal-security facility while the potentially acid-generating minerals are placed in a high-security facility.

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Chapter 31

Retreatment of gold residues

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1. INTRODUCTION

Although this chapter provides a generic overview of the subject, it is largely influenced by the authors' experience in processing of sand and slimes dumps at the Ergo operation owned by AngloGold Ashanti in South Africa. It is therefore specifically aimed at gold recovery from a mixture of sulfide and non-sulfide bearing residues which arose from mining activities on the Witwatersrand from the early 1900s until the mid 1960s.

The chapter deals exclusively with gold and sulfur recovery although Ergo produced uranium for a period and continues to produce both sulfuric acid and oleum as by-products. The reclamation methods and general processing techniques would, however, be applicable to recovery of other minerals although the specific flowsheets would obviously differ.

Gold-mining residues typically fall into one of three categories comprising slime (particle size of about 75% passing 74 μm), sand (about 10–20% passing 74 μm) and waste rock. Since the slime and sand has been previously processed, it typically has a low gold grade (<1.0 g/t) and will provide relatively low recovery efficiencies, in the order of 50%. Waste rock will also be of low grade (<0.8 g/t) but may exhibit the potential for higher recovery once milled. The retreatment of waste rock is not covered in this chapter.

Since the cost of mining and size reduction (partial in the case of sand) has already been incurred, these residue materials normally constitute a 'cheap'

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*Retired

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source of gold, especially when exploited as a tonnage make up to fill excess treatment capacity within an existing processing facility. In this scenario, the sand or slime can be processed at marginal treatment cost and can make a substantial contribution to the bottom line profit of an operation.

The prime justification for residue retreatment will always be to create a profit for the company concerned. Other benefits to be considered could include release of land for urban development and removal of 'environmentally unfriendly' dumps (and their associated long-term liability) for relocation to a more modern facility.

2. EVALUATION PHASES

When the reprocessing of residue deposits is being considered, it is necessary to obtain credible information about the resource in order to generate quality feasibility studies that will be used to determine the financial attractiveness of the project. This information may be collected from a number of sources, including historical records, but it is strongly recommended that a formal evaluation process be undertaken to establish the validity of available information.

The evaluation techniques for slime/sand deposits involve sampling, assaying, metallurgical testwork and grade/tonnage calculation. The extent and complexity of the sampling programme (and the subsequent metallurgical testwork) will vary depending on the quality of information initially available, the complexity of the resource characteristics and the degree of risk involved in the project.

2.1. Scouting

This first step in evaluation is normally used as a preliminary screen to establish whether a resource has any potential or can be eliminated without any significant expenditure being undertaken. Sampling would normally comprise simple grab sampling with reasonable care being taken to ensure appropriate coverage of the deposit. The objective of this stage is to quantify the potential of the deposit and it will not produce any concrete findings as to the financial viability of processing the material. The required outcome from this stage will be a recommendation either to proceed to a more detailed evaluation or to abandon the project.

Metallurgical testwork for this first stage would be limited to assaying for gold and sulfur, and leaching composite samples (after pre-aeration) for 18 h in excess cyanide (up to 2 kg/t to ensure complete dissolution). It is preferable to conduct two sets of tests, with and without carbon (30 g/t), to establish the presence and effect of *preg-robbers* and the response to carbon-in-leach (CIL) conditions.

2.2. Pre-feasibility study

The next level of evaluation will be introduced only if justified by the scouting testwork. The pre-feasibility study requires more detailed information and, hence, specific sampling and testwork procedures need to be developed.

3. SAMPLING AND METALLURGICAL TESTWORK

The sampling programme must be developed with due consideration being given to the characteristics of the site and the resource material. The normal sampling grid for large slimes dams is 200 m spacing. However, this may be increased or decreased according to the size and detail of the dam.

The grid must be of a size and orientation such that it will not place an excessive number of sampling points on the walls of the dam or next to historical feed points. Experience has shown these sites to be potential sources of bias since they can represent areas of concentration, which arise during the dam construction process. A further *wall effect* relates to the oxidation of the outer 2–3 m of slimes in a dam with a resultant loss of sulfide sulfur. On a high sulfur grade dam the overall sulfur grade may be biased downwards as a result of this effect. The sampling programme must therefore sample the walls in proportion to the total tonnage contained in the walls compared to the total resource tonnage. Isolated pockets of slime, toe walls, toe paddocks, marshy areas and run-off slimes are sampled on a smaller grid than the main dam.

Sand dumps, due to their structural shape, are sampled on a smaller grid than slimes dams and, as sand generally has a lower sulfur grade, the wall effect can be ignored.

The sample points are set out and marked on the slimes dam by a land surveyor using a GPS system. The Y and X co-ordinates of each point and the collar elevation are measured and recorded. Every sample point is plotted on the survey map and is given a consecutive number that is matched to a sample number and, hence, to a gold and sulfur grade. From the collar elevation and the depth of the slime to ground level the contour of the underlying ground can be determined.

A hand auger can be used on material with a depth of less than 2 m. Deeper holes require an hydraulically driven sleeved auger, which normally drills a 50 mm diameter hole. The borehole is drilled and sampled in 1.5 m increments to provide suitable information on grade variation throughout the height of the dump.

Due to the fact that sleeved-auger drilled boreholes are not lined, the depth of the hole may be affected by the sand/slime stability at depth. However, holes as deep as 35–40 m may be achieved in favourable conditions. The moisture content and particle size are two factors that influence the stability of the material being drilled.

Sand, being coarser than slime, is more likely to collapse and close the hole at depths exceeding 25–30 m. Similarly, very wet slime (+30% moisture) will not support itself and the hole will close as the auger is withdrawn. Because the moisture content of the slime within the same dam may vary greatly, one borehole may reach ground level where an adjacent hole will not.

When sampling down to ground level of a deposit cannot be achieved due to drilling constraints, the calculated grade of the dump may be lower than the actual *in situ* grade due to incomplete sampling of the bottom of the dump. The base of the dump often has an enriched base layer, particularly so in the case of sand dumps. It is also important to collect the first 0.5 m of soil as a separate sample for grade analysis to determine whether gold has migrated into the underlying surface.

Dams containing rock or other physical entrainments are very difficult to sample down to ground level. Generally, on a clean slimes dam 85% of the boreholes will reach ground with relative ease. Other sampling techniques that may be used for sampling shallow sand/slime that is contaminated with rock, rubble or refuse include digging of trenches or pits.

Each 1.5 m sample increment is bagged and retained as a discreet sample. The auger flights are cleaned after each sample has been removed to prevent contamination of the subsequent sample. The sample bags are sealed and labelled with a ticket number, borehole number, slimes dam name and depth. A comprehensive drilling logsheet is generated for each sampling campaign.

Drilling campaigns are conducted under the supervision of a professional person to ensure the integrity of the samples. When a third party who has some vested interest in the material samples, the deposit should be randomly sampled again by the processing party for comparison with the original samples.

3.1. Sample preparation

The first stage of sample preparation is to thoroughly mix each incremental sample to ensure homogeneity. A sub-sample taken from each incremental sample is submitted for gold and sulfur determination and other analyses as required. The remainder of each incremental sample is split into two portions with one portion being retained in reserve and the other portion being combined with all the other incremental portions to make a single borehole composite sample. A sub-sample, proportional in size to the depth of each borehole, is taken and combined with the other sub-samples to make a single dam composite sample representative of the entire dam. The remainder of the original borehole composite samples are kept in reserve. The dam composite sample is sub-sampled for gold, sulfur and other relevant analyses as well as for metallurgical testwork. The soil samples from each borehole are separately mixed and assayed for gold and sulfur.

The preparation steps described above will result in borehole and dam composite samples that are representative of the material on a vertical plane. Composites can also be prepared to provide a horizontal representation, if required. Likewise composites can be generated for groups of boreholes representing different areas of a dam (high-grade areas, sand/slime areas, specific cross section areas, *etc*.), depending on the complexity of the deposit.

The samples should be stored in their naturally arising damp condition in sealed bags or containers, as these materials frequently have high oxygen demand and can start to oxidize on exposure to air. Stored samples have a finite shelf life of about 3 months, by which time they have oxidized to the point where they are no longer suitable for testwork and are discarded. The storage of samples under nitrogen or inert gas should be considered if oxygen demand is anticipated to be high.

It is important to note that the samples for metallurgical testwork should not be dried, as drying before testwork almost always gives enhanced recoveries and, thus, results in an over-estimation of the potential of the resource.

3.2. Assaying

As described, incremental and borehole samples are assayed for gold and sulfur. The overall dam composite sample is assayed for gold, sulfur and other elements of interest. Where a slime deposit interfaces with a sand deposit, the incremental samples that contain both sand and slime can be screened and the gold grade of both the sand and slime fractions determined.

Assaying must be done at a reputable laboratory and should include duplicates, blanks and known standards to monitor the analytical accuracy and possibility of sample tampering.

3.3. Metallurgical testwork

The testwork programme should be designed to allow the most economically effective treatment route to be selected. A variety of metallurgical testwork is done on slimes/sand samples, including direct gold leach; sand milling; cyanide, lime and oxygen demand; *in situ* moisture content and pH; settling characteristics; and size analysis. A high sulfur-grade dam would be subjected to flotation testwork, which may include flotation recovery of gold and sulfur; roasting; flotation tailings gold leach; and calcine gold leach. The testwork programme has to be designed to incorporate the relevant tests from this list depending on the most likely processing scenario.

Samples should not be dried in an oven as this has been shown to enhance gold leach recovery. Material for leach testwork is, therefore, not dried but kept as a moist filter cake. Marshy material, which has a high organic content, and residue material from a plant operating a carbon circuit must also be tested for potential *preg-robbing*.

The tests proposed below are not exhaustive, and not all the tests are required if the local conditions drive the flowsheet selection in a particular direction. The recommended tests should be conducted in a selected sequence in order to reduce costs. This will allow one to direct the remainder of the testwork programme in a logical manner.

The following tests should be considered when designing the testwork programme:

- Scouting tests to determine lime, cyanide and oxygen requirements
- Kinetic tests to establish residual cyanide and lime levels
- Direct leach (lime, cyanide and dissolved oxygen >8 ppm)
- Direct leach (no oxygen addition)
- Direct leach (2-h pre-aeration)
- CIL (at optimum reagent additions with 30 g/L carbon addition)
- Extraction rate (for optimum route determination)
- Mixed feed ratio tests where a number of sites will be reclaimed
- Settling tests
- Size distribution and gold deportment
- Presence of preg-robbing species
- Viscosity of the resultant slurry (may cause floating of carbon in the CIL circuit)
- Flotation testwork, gold leach on pyrite concentrate and flotation tails
- Roasting of pyrite and calcine gold leach.

An important consideration is that residue deposits often contain significant amounts of surface-precipitated aurocyanide, which will dissolve easily. Thus, in all testwork, gold in solution must be determined and combined with gold on solids to give the total gold grade.

4. EVALUATION

4.1. Flowsheet development

Once the testwork results are known, a formal flowsheet can be developed based on the unit processes required, the scale of the operation, expected reagent requirements and so on. The key aspects of flowsheet design are likely to be the method of reclamation to be employed (hydraulic or mechanical); the need for milling; the necessity to incorporate a flotation step, with subsequent pyrite treatment (leach or roast and leach calcine) and flotation tails leach, and type of gold circuit (*e.g.*, CIL).

The design also needs to take cognizance of any existing under-utilized or redundant plant available through which the material could be processed. The location and size of the resource may impact on the process route to be evaluated. The reduction of infrastructure costs to achieve economic optimum may be achieved by utilizing the existing infrastructure of the nearest plant, even if this does not provide the maximum recovery factor.

Operating costs can now be predicted to a greater degree of accuracy and used in the financial evaluation, which is incorporated into the feasibility study.

4.2. Tonnage and grade calculation

The tonnage of the resource is calculated using simple volume and *in situ* density information. Surface areas may be surveyed, measured from a scale map or aerial photograph or measured with a measuring wheel. The depth of the slime/sand is calculated from the borehole depths or ground contour. Typical slime dry *in situ* density is 1.47 t/m^3 and sand is normally 1.40 t/m^3.

It is important that the entire footprint of a slime/sand deposit is identified and delineated. The footprint, which includes run-off material and other areas of slime associated with the main deposit, is used for tonnage calculations and the setting out of permit boundaries. Aerial or satellite-scaled photographs are an excellent means of determining the footprint of a deposit.

Gold and sulfur grades are determined from the borehole drilling grades that are always weighted to ensure an accurate calculation. An extrapolated grade can be calculated for those boreholes that do not reach ground level provided there are values from other holes in the proximity. Grade extrapolation must be the exception rather the rule and should be used conservatively.

Grade dilution and its possible effect on profitability and measurement must be considered at this stage. Grade dilution occurs when high-grade material is blended with low-grade or barren material to such an extent that the overall feed grade to a metallurgical plant is reduced and the processed tonnage increased. This dilution can occur during the mining operation when so-called *undercutting* takes place during hydraulic and mechanical reclamation. The degree to which this affects the grade is largely influenced by the nature of the sub-base material and the 'cleanliness' of the mining techniques involved. Ergo recently introduced a more mobile monitor gun (the *excavator gun*) to minimize dilution caused during bulldozing and other mechanical floor clean-up operations (Fig. 1). An estimate of this dilution effect must be allowed for in the financial model and it should be noted that this becomes more of a problem towards the end of life of the operation. There is typically

Fig. 1. Excavator-mounted monitor gun.

minimal dilution under normal reclamation operations but this may rise to as much as 30% when conducting final floor clean-up operations.

4.3. Size distribution

As previously noted, the testwork includes determination of the size distribution of the resource. This enables identification of the material as slime, sand or a mixture and this will influence the reclamation method and treatment route. It is normally accepted that the slime pumping, piping and treatment facilities can tolerate up to 10% sand in slime, but this needs to be carefully controlled to ensure that excessive amounts of sand are not slugged into the system.

The bottom level of a slimes dam will tend to be coarser than the average for the dam, with this effect compounded by the coarseness of the underlying ground material. This size segregation and ground coarseness will impact on the ability to reclaim the bottom slime level and on final clean-up activities due to the rapid settling of coarse particles in the launders of a hydraulic reclamation system.

Sand will normally require some degree of milling prior to either direct treatment or combination with either reclaimed slimes or ore.

4.4. General observations

In addition to the formal testwork, it is important to include additional observations made on site. These may influence the final flowsheet and financial model, which are incorporated into the evaluation report.

Of particular importance is the presence of contamination within the resource, which may hamper reclamation operations or impact on the efficiency of the treatment process. The presence of rock (possibly from previous cladding or buttressing efforts) in or on the dam will interfere with the sample drilling, will impede hydraulic reclamation (and reduce daily tonnage) and will involve additional costs for removal of the rock.

Dams that have been used as mine, municipal or industrial waste disposal sites will require special attention as foreign material in the dam will also impede sampling and involve removal and disposal costs. Certain wastes such as fibreglass and plastics have caused major reclamation problems due to their ability to choke screens, valves or pumps and have even resulted in *furring* of transport piping, causing reduced production and requiring costly pigging of pipes to restore the production capacity.

Chemical and organic waste (including sewage and animal/abattoir waste) can lead to accelerated pipe and equipment corrosion, high oxygen, lime and cyanide demand and surface coating of particles, leading to low recovery. The identification of contaminants during the resource evaluation stage is, therefore, extremely important as these may render processing of the resource economically unattractive. Furthermore, the contaminants will result in a removal cost and possibly represent an environmental problem.

4.5. Financial evaluation

All of the collected information (together with assumptions on revenue prices, future escalation, *etc.*) is then fed into a financial model covering the life of the resource. This model will calculate the net present value (NPV) and rates of return for the project. All costs associated with the project including acquisition costs, capital expenditure for infrastructure and operational costs have to be included in the financial model. Environmental costs should also not be overlooked. These include the cost of site rehabilitation to final closure standard for the reclaimed dam footprint, demolition and clean-up costs for the reclamation and processing infrastructure and final closure of the tailings-storage facility (see Chapter 11 for a more detailed discussion of dam closure issues).

4.6. Infrastructure requirements

An optimum flowsheet will have been determined via the metallurgical testwork and in order to size the equipment correctly, the required throughput must be determined. The optimum throughput for the operation will be influenced by the size and grade of reserves as well as the impact of throughput rate on project life, capital cost and the effect of *economy of scale* on operating costs. It is generally accepted that these low-grade operations need to be volume-driven in order to generate acceptable returns. A number of different throughputs have to be tested via the financial model in order to establish which throughput rate gives the best balance of capital input, operating cost and return.

In preparing preliminary cost estimates it is normal to source information from operations with a similar process and technology. Sensitivity calculations evaluating the financial impact of variations in revenue and costs will also assist the decision-making process. Other important considerations that influence the infrastructure requirements include the availability of services such as water, power and access roads; the selected reclamation strategy (hydraulic versus mechanical); the physical location of resources with regard to their proximity to each other, and their proximity to existing treatment facilities.

4.7. Environmental costs

Rehabilitation and closure costs must also be built into the financial evaluation. Historically, rehabilitation costs were minor. However, with the passing of time, environmental standards have become highly legislated, controlled and therefore costly to adhere to. These costs are liable to escalate into the future and it is therefore essential that sensible rehabilitation costs be built in to the resource evaluation.

In the event of the dumps in question being owned by the processing company, a portion of the project cost may be offset against activities that would have had to be conducted in any event as part of the company's liability for environmental rehabilitation. These constitute a committed cost as far as the operation is concerned and care should be taken to avoid 'double accounting' for these costs, although the timing of the expenditure will change to meet project requirements.

4.8. Operating costs

All costs incurred due to the treatment of the resource need to be allowed for in the determination of its financial feasibility. Based on the testwork and size of the operation, expert consultants and engineering contractor organizations could assist in advising an operating cost based on their experience and drawing on information from other similar operations.

The foregoing work would conclude in a formal pre-feasibility study report covering all aspects of the project. If the pre-feasibility shows acceptable NPV and rate of return, it is then a management decision as to whether a further stage of feasibility is justified or necessary regarding proceeding or terminating the project. The subsequent feasibility study would be developed through a process of more detailed engineering drawings, specific equipment lists, tender prices and so on.

5. OPERATIONAL PHASE

5.1. Reclamation methods overview

There are three main methods of reclaiming the material from the resource, namely hydraulic re-mining using high-pressure water-monitor guns, mechanical reclamation and dredging.

Hydraulic re-mining is generally best suited to slime reclamation and is not as well suited to sand reclamation due to the tendency of sand to settle out in the launders from the face to the pump station. Mechanical reclamation is conversely better suited to sand reclamation and is an expensive option for slime due to its tendency to choke up transfer points on a mechanical reclamation system. Dredging is generally very expensive and only used in specialized applications where hydraulic or mechanical re-mining is not possible. An example of this would be reclamation from a waterlogged marsh area, where drainage to facilitate mechanical or hydraulic mining is not feasible.

Potential reclamation challenges need to be identified and considered during the evaluation phase. These challenges could include high, low or variable *in situ* density; presence of solid contaminants such as rocks or scrap; flat or very steep topography; and the presence of watercourses. These factors can impact directly on the reclamation process selection and must be properly identified, quantified and considered during the evaluation phase as they directly influence the capital and treatment costs of the project.

An overview of the advantages and disadvantages of the various reclamation techniques is given in Tables 1–3.

Mechanical reclamation involves earth-moving equipment such as bulldozers, front-end loaders and trucks, which load and haul or convey the material to a screening and re-pulping system. Bucket wheel reclaimers with conveyor transfer systems have been used on several operations with varying degrees of success. Front-end loader and trucking would only be considered for very small deposits, which could not carry the capital cost of a more substantial installation.

Dredging (underwater reclamation) is expensive due to the high cost of the equipment required to carry out this work. It is also more challenging from an environmental perspective although it may be preferable to other options such as river diversions. Drainage of the site (during a dry season if possible) is the preferred option due to cost and manageability issues, with dredging being a recommended approach where drainage is not possible.

After draining, a decision to monitor or truck the material would be dependent on a site-specific evaluation. If there is a favourable face height then monitoring should be the preferred option. The underfoot conditions should be examined carefully to prevent the sinking of expensive machinery.

Table 1
Hydraulic re-mining advantages and disadvantages

Advantages	Disadvantages
Comparatively low operating cost	Inability to reclaim all material due to uneven floor profile. Some degree of mechanical reclamation will be required for final clean-up
Ability to control pulp density and flow by varying number of guns operating and nozzle size	Requires extensive trench and launder excavations
Uses gravity flow to pump station reducing energy costs	Satellite pump stations will be required in low-lying areas of the floor
Simple, low-tech processing systems, *i.e.*, screening, pumping and pipelines	Significant impact of rainfall on operation due to dilution at site
	More difficult to separate non-pay material from pay material

Table 2
Mechanical reclamation advantages and disadvantages

Advantages	Disadvantages
Clean up to ground floor possible	Comparatively high reclamation cost
Can segregate non-payable material to be left *in situ*	Firm ground surface required to support earth-moving machinery
	Higher recovered grades are required to make this method cost effective

It is worth noting that estimating the tonnage reclaimed from underwater reclamation is often difficult and, as a consequence, the efficiency of the operation may be difficult to evaluate. Due to the soft underfoot condition of a water-filled dam, a clean separation between slime and base material is unlikely. This will lead to grade dilution of up to 30% and equivalent tonnage and operating cost increase.

5.2. Slime reclamation by hydraulic re-mining

Slime reclamation by hydraulic re-mining involves recycling water from the treatment complex to booster pump stations from where it is delivered at high pressure directly to the monitor guns at the reclamation sites (Fig. 2). These guns direct high-pressure water jets at the slimes dam face. The resultant

Table 3
Dredging advantages and disadvantages

Advantages	Disadvantages
No major changes to water reticulation or elimination of water inflows to the site to be reclaimed	High site establishment and de-establishment cost for equipment
Reclamation can be done with no impact of seasonal changes, *i.e.*, rainfall and storm water control	Not all material will be reclaimed due to the mechanical action of the dredger, which causes material to 'fluff up' and be missed by the dredger
Minimizes water disturbance and consumption	Contract normally volume based
Best suited to reclamation of material beneath swamps or lakes	Dredger inlet choking due to vegetation on site
Effective in areas of poor bearing-capacity where mechanical equipment would sink	Low reclaimed density compared with other methods
	High total cost of reclamation

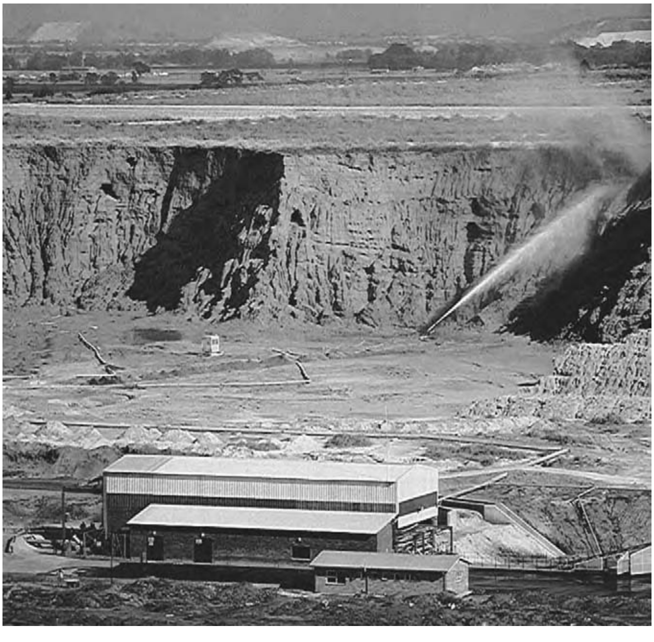

Fig. 2. Reclamation site showing remote monitor gun with main transfer station in the foreground.

slurry gravitates via earth launders, with finger screens installed to trap coarse trash and vegetation, to a transfer pump station adjacent to each dam.

The pump station is located at the lowest point on the perimeter of the dam allowing as much as possible of the dam material to gravitate to the screening and pumping station. In-dam satellite stations may be required to reclaim any remaining slime in low-lying areas.

After screening to remove coarse trash (typically +2 mm), the slurry is pumped to the treatment complex with the assistance of booster pump stations when pumping distances are long. The screen oversize, which consists mainly of vegetation and hard lumps of slime, is deposited on nearby sites where the stockpile can be rehabilitated at closure.

In order to prevent contaminated or polluted water from leaving the site in an uncontrolled manner, provision has to be made for emergency dams into which any storm water or other excess run-off can be diverted. Slime carried into these emergency dams has to be subsequently reclaimed.

5.2.1. *Starting a reclamation operation*

An area of the dam wall next to the pump station is mechanically excavated to serve as a catchment area. The dam wall is re-instituted with two piped outlets through the wall for movement of slurry (lower outlet) and rainwater (upper outlet). These are valved to avoid uncontrolled flood release, which can be held in the catchment. Normal reclamation then begins from the selected start point with the slurry flowing via the catchment area, through the slurry control valve to the pump station.

5.2.2. *Reclamation technique*

Where possible, dams should be reclaimed in a down-slope manner starting from a point furthest from the pump station and advancing down the slope until the resource is exhausted. Experience has shown that a slope of 1 in 150 will provide adequate slime flow without settling of coarse particles.

Well-cut launders prevent the slime from *meandering*. Meandering creates slime build-up, which can require future clean-up. This measure, together with ongoing ground cleanup (*i.e.*, while reclamation is underway) to the required closure standard, has been shown to minimize final site rehabilitation costs. The ongoing clean-up approach also ensures that the low-density stream associated with clean-up activities can be carried by the main dam reclamation tonnage, thus minimizing adverse production impact towards the end of the operation. Should this ongoing clean-up philosophy not be followed, then final clean-up will involve either low density tonnage reclamation, which may be inconsistent with the pump/piping capability, or mechanical scraping and piling of material into sizable reclamation piles, both of which are costly exercises. Other advantages are that equipment may be removed for reuse at other sites and that rainwater falling on a cleaned site can be allowed to run naturally off site with no adverse effect on production.

Rainwater falling on an operating site will be classified as process water and is not suitable for release into the surrounding environment. Attempts should be made to contain this water in paddock areas for evaporation or controlled release to minimize its effect on production.

Two hydraulic reclamation methods are commonly used, namely, *full-face* or *step-cutting* (*benching*). Full-face reclamation employs guns remotely operated from a cabin distant from the gun position. Benching uses guns manually operated by a person standing at the gun who directs the stream of water.

For full-face reclamation, the use of remotely controlled guns can result in labour savings when compared with benching. Better control of slurry density can be achieved through the use of a programmed washing pattern (which is more reliable than manual control). A programme can accommodate *figure-of-eight* patterns plus up–down and left–right patterns without jeopardizing face integrity. Due to large gun and pipe sizes involved with full-face reclamation these units would be moved by mechanical means.

As the full face of the dam is being reclaimed, the gold grade will tend to be less variable than with a benching technique, where isolated low-grade layers may be exposed for a period. Due to the face height involved in full-face operations, it is important to create a safe face-working angle to prevent damaging and hazardous face slides. This is achieved by using the guns from ground level, in a step-cutting procedure whereby the top of the dam face is cut down to remove the top of the face. The top quarter and second quarters are progressively cut away before cutting the bottom levels.

The benching technique essentially removes the dam in layers progressively from the top level working down with the layers being up to 5 m in height. The guns are located on the top surface of the dam and moved to the lower bench levels as the reclamation proceeds.

The benching technique, which uses lighter piping (easily joined) and hand-manoeuvrable guns, is more labour-intensive and has poorer working conditions compared with the full-face operation. Grade may also be more variable due different layers of the dam having different grades. The benching system tends to require more faces in operation at any given time compared with a site operating on full-face. The operation of multiple faces makes management, planning and stormwater control more complicated. Benching tends to progressively reduce the overall height of the resource, whereas full-face operations progressively reduce the area of the resource. Ground clean-up activities, which rely on the release of cleared land, are therefore more easily managed in a full-face reclamation operation. Benching will result in a low face/large area operation at the end of the project life that can impact on both production and costs. The size of benching equipment is suited to operations with low face.

A further consideration in reclamation methodology is dam stability. If the dam has stability problems, full-face monitoring may prove to be too hazardous and the benching technique should then be employed. In all other cases full-face reclamation is the preferred reclamation method.

5.2.3. Monitor guns

The guns deliver a high-pressure water jet that is directed at the working slimes-dam face (Fig. 3). The guns are up to 150 mm diameter fitted with 40–60 mm nozzles and the guns operate at a pressure of 20–30 bar. The nozzle diameter may be adjusted as appropriate for the material and tonnage being reclaimed. The guns must incorporate a device to lock the guns when not in use and the gun barrels should be placed in an upward position when the water feed valves are being opened. On start up, there is the potential for water hammer in the water feed-line, which can cause uncontrolled recoils and movement of the gun. Gun design should therefore incorporate a mechanical stop to prevent the uncontrolled movement of the gun outside of a prescribed arc and operators should stand clear of the gun at start up.

In full-face operation, the gun should be positioned at a maximum distance of 50 m from the face and the gun control cabin should be at least 120 m from the working face and offset at an angle to the working face. This is to ensure that the cabin is out of the direct line of any potential slide. A small retaining wall (*berm*) should be built between the face and the cabin.

Fig. 3. Manually controlled monitor gun.

A resting period of one day should be allowed between operating and moving a gun closer to the face as this will give time for potential slides to occur before the crew moves the gun into what could otherwise be a hazardous location. This should only done on day shift and under direct supervision.

5.2.4. Screening

Finger screens are installed in the earth launders to entrap and remove refuse, vegetation and other trash to 50 mm in size (Fig. 4). Where possible these should be installed in line with the flow in such a way as to introduce a degree of self-cleaning. The slurry also flows over vibrating screens to remove >2 mm material at the pump station (it may be necessary to pump onto this screen). This removes coarse material, which may damage the pumps, pipes and valves in the slurry delivery system. As much as possible of any surface vegetation, refuse and physical contaminants should be mechanically removed prior to reclamation monitoring, to avoid launder chokes and screen overloading.

Fig. 4. Finger screen installation.

5.2.5. Pump stations

The transfer pump station at the reclamation site will involve multi-stage slurry pumps which pump the slurry to the treatment plant via an overland delivery pipeline, with intermediate booster pump stations if the distance to the plant is very long (Fig. 5).

These pump stations also incorporate the water pumps which supply the high-pressure water for monitoring use. The pump stations normally have operating and standby sets of both slurry and water pumps.

Satellite pump stations may be required to remove material from areas on the dam that are lower than the transfer pump-station (Fig. 6). These could be located *in dam* or on the perimeter, depending on the topography of the site. The operation of the satellite station involves the creation of a small pumping sump, which simply transfers the slurry to the main pump station. As with the main pump station, it is normal to install static screens in the feed launders to minimize the choking of pipelines and pumps from the satellite to the main pump station.

While satellite stations are effective in removing small amounts of material from difficult areas at low capital cost, operation is generally labour-intensive.

Vertical spindle pumps are the preferred choice for satellite pumping as they are simple to install and can handle large volumes of solids. An option that has proved successful over the years at Ergo is the use of a tank satellite placed in the catchment, where the pumping system is placed inside a tank.

Fig. 5. Main transfer pump-station.

Fig. 6. Satellite pump-station (pump placed inside redundant tank which is sunk into the catchment area).

5.2.6. Pipelines

Slime should be pumped at a velocity of 1.9 m/s or lower in an unlined steel pipe. This has been shown to give an optimal balance between tonnage throughput and pipe wear. At velocities greater than 2 m/s it is recommended that a rubber-lined pipe be used (concrete lining has been used at Ergo but is not recommended for long-life operations due to erosion of the concrete in areas where the lining application is not even). At 1.9 m/s pumping velocity, 10-mm-thick mild steel should provide a life of up to 15 years, depending on the size distribution and abrasiveness of the material being pumped. The life of a rubber-lined pipe is approximately three times the life of a steel pipe if pumping slime in a similar situation. When pumping slime containing more than 10% sand a rubber-lined pipe must be used. The cost of rubber-lined pipe is typically 50% higher for a 25 bar duty pipe and 37% more for 10 bar duty pipe when compared with steel pipe.

Rubber-lined pipes should also be used in situations where the pH of the reclaimed slime is below 5, where metals capable of precipitating and forming micro-galvanic cells on the pipe wall exist or if sulfur-reducing bacteria could be a problem.

Pipes should not be placed on steel or concrete plinths since movement of the pipe on the plinth (due to expansion and contraction) causes abrasion wear at the plinth to pipe contact point, resulting in failure. If plinths must be used, timber or some other soft surface should be used, although it is recommended that pipes be placed on the ground where possible.

Pipes crossing sensitive areas such as roads, railway lines, power lines, other pipes such as gas or potable water, water courses, wetlands, parks and so on should be rubber-lined to minimize the potential for failure. In such areas it is also recommended that provision be made for easy removal of the pipe and space provided for standby piping so that minimum production interruption is caused by any pipe failures. Pipes crossing or running parallel to railway lines or marshy or wet areas have to be protected against stray electrical currents by electrical bonding and cathodic protection systems.

Pipelines should have test sections fitted. These can be periodically removed for inspection for signs of corrosion, erosion and scaling. Ultrasonic thickness testing should be regularly conducted to ensure that pipe integrity is being maintained.

Although pipe lengths are normally welded together rather than flanged, occasional flanging is necessary on bends and at isolation points. When a pipe is opened at flanges on long pipeline sections it will spring apart due to the inherent stress in the pipe. The provision of distance pieces of various lengths with flanges will facilitate the reconnection of opened pipes.

Pressure control and pressure release valves should be installed in the pump stations on monitor-water pipelines when high pressure (potential energy) could pose a danger to workers in the area. The use of gate valves, rather than ball or butterfly valves, should be considered, as they are more effective in controlling pressure in the line.

Depending on the alkalinity and scaling potential of the monitor water, it may prove necessary to add antiscalant into the monitor water system. This is stage injected into the water pipeline with a total addition of about 4 mg/L usually proving sufficient. Both the main slurry and monitor water pipelines should, in any event, incorporate a facility to allow pigging on a regular basis to remove scale build up and retain capacity without major impact on production.

5.2.7. Water balance

The water balance for a slimes reclamation circuit employing hydraulic remining needs constant awareness, monitoring and control. Consistent water inputs in terms of quantity and quality are required for the monitoring feed system to ensure that steady pressures are maintained at the face. If the process involves a flotation circuit, dilution water to achieve an acceptable density for flotation may be required. Similarly, incorporating a roaster and acid plant into the circuit will create a water demand for gas cooling/cleaning, calcine cooling and slurrying.

Since the water volumes involved are large for a high tonnage operation, it is essential to reuse water in order to reduce the consumption of expensive potable water and to avoid water build-up, which can lead to environmental problems. Re-circulated water originates from the plant thickener overflow and from the return-water system at the final deposition site. Rainwater falling on reclamation sites and tailings dam basins is also captured and added to the process-water system. Therefore, it is necessary to monitor and control external water addition into the circuit to avoid build-up of the total water inventory. The major water-loss mechanism is the water retention within the settled bed in the final tailings-dam.

Some process water could contain minor residual levels of cyanide, which could depress flotation response, and this must be allowed for during the flowsheet design.

As previously mentioned, due to the minor amounts of cyanide in the process water and the precipitated nature of some of the gold in the resource, reclaimed slime will contain appreciable levels (up to 20%) of dissolved gold before it even reaches the processing facility. This needs to be measured and reflected in the gold accounting system with care taken that recirculating soluble gold is not double accounted.

It has been demonstrated that leaching continues (at low levels) on the CIL residues during pumping to the dam and on the beach. For a large operation it may be justified to install separate carbon columns on the tailings-dam return-water system to recover any residual dissolved gold that may be present. The carbon from these columns simply becomes part of the overall CIL carbon circuit.

It is not possible to use a carbon-column system on the thickener overflow if unstable calcium sulfate salts are present as these may scale up the column and carbon in just a few hours. This does not happen when treating the tailings-dam return as the calcium sulfate has stabilized due to retention time on the dam.

5.2.8. Reclamation guidelines

These guidelines highlight key issues and important aspects that should be considered when setting up the operation.

- The full-face reclamation technique becomes potentially more difficult as face height increases and this has to be managed by close focus on the angle of cut and cabin distance from the face. The higher the face is, the more cost effective the full-face technique becomes, but this must be balanced with increased risk due to face stability problems.

- The company must retain management of the reclamation sites even if a sub-contractor carries out the reclamation activities. Similarly, the processing company will always retain all liabilities and rehabilitation costs.
- Stability of reclamation sites must be routinely monitored to establish whether the risk profile is increasing as a result of the activities on the site. Relevant topics include the vertical dam face profile, existence of tension cracks (*slip circles*) on top of the dam and *ponding* of water around the reclamation site. In general any changes from the 'normal' condition of the dam must be evaluated to identify any increased risk.
- Shear failure through a slimes dam occurs when a section of the slime slides on a curved surface (arc) or on a linear surface (wedge). The stability of the slimes face is assessed by considering a number of possible failure arcs and determining the lowest factor of safety against slipping. The critical arc is that with the lowest factor of safety against failure, *i.e.*, the highest probability of failure. These evaluations are usually best handled by professional third-party geotechnical engineering companies that have experience in the field of tailings dam construction. The important geo-technical parameters that influence stability are unit weights, cohesion intercepts, friction angles and position of the phreatic surface. It is important to obtain the appropriate information regarding gold slime and compare it to the associated sub-soils.

5.3. Sand reclamation and milling

5.3.1. Hydraulic reclamation

Hydraulic re-mining of sand can be done and is practiced at a number of operations. However, it is not the favoured option for sand as the coarse nature of the material requires steep launder slopes (of the order of 1 in 50). This is to ensure adequate slurry velocity and prevent the particles from settling out and choking the launders. This results in a requirement for extremely deep launders over the length of the deposit. Since this is not really practical, mobile satellite pump-stations are required to follow the moving face and maintain an acceptable launder depth or pump the slurry directly to the transfer pump-station. The guns also need to be close to the face being reclaimed. This can all be done but it results in a cumbersome, mechanically complex and labour-intensive operation. Therefore, the preferred route of sand reclamation is by mechanical means.

5.3.2. Mechanical reclamation of sand

Bulldozers and front-end loaders remove the sand from the dump and load it on to a system of conveyor belts and transfer chutes. These deliver the dry sand to a screening and slurrying section, which is where the coarse oversize and grit is removed in a multi-stage screening process (normally wet screening for the finer screen sizes).

This slurried sand is then pumped to the milling plant. The slurry would be pumped in rubber-lined steel pipes at a density of 1.45–1.55 t/m^3 and a velocity of 2.1–2.4 m/s. The slurry can be pumped for considerable distance if required.

5.3.3. Milling of sand

Location of the milling plant will be project-specific and is dependent on the geographic layout of the project resources in relation to available milling infrastructure and utilities. The milling section could be located at the main processing facility or at a remote location, depending on the most convenient and cost-effective arrangement. The milling circuit would typically employ overflow ball-mills operating at about 70% of critical speed with a grinding media of 50 mm balls. Once the sand has been milled it becomes slime and can be mixed with other slime for processing.

The slurried sand is pumped from a stock tank into the milling-circuit primary sump from where it is pumped to the primary cyclone classification circuit. The underflow gravitates to the mill and the overflow reports to the secondary cyclone. Underflow from the secondary cyclone reports back to the primary sump for re-circulation together with the mill discharge and new feed, while the overflow discharges into the secondary sump.

From the secondary sump, the slurry is pumped to a de-watering cyclone cluster, which is designed to discharge a consistent underflow product at a relative density of 1.40 t/m^3, which is then pumped to the processing plant. De-watering cyclone overflow reports back to the primary sump to supplement the dilution water added at this point. The use of de-watering cyclones provides an underflow density suitable for downstream treatment processes and enables return of water via the overflow back into the milling circuit.

A flowsheet of sand reclamation and milling is included as Fig. 8 at the end of this chapter.

6. METALLURGICAL TREATMENT

6.1. Slime treatment with no pyrite recovery

The low grade of the incoming slime will necessitate a high-volume throughput to provide economy of scale and enhance profitability. A relatively short leach residence time in the order of 8 h will probably provide an optimum return on the project.

The reclaimed slime would normally be received at the treatment facility at a relative density of 1.40–1.50 t/m^3. However, reclamation methods, stop/start periods, flushing of lines for maintenance, *wetness* of *in situ* slime, low monitor-water pressure, *flaring* of the water jets due to nozzle wear, surface clean-up operations, and, in particular, heavy rainfall can cause a much lower incoming density to be achieved (especially on a short-term basis where large fluctuations in the incoming density can arise). In the event of heavy rainfall the reclamation site may be flooded and, as a result, only water or very dilute slime would be pumped to the plant while recovering the reclamation site. Rainwater falling on to an uncleaned reclamation site is considered to be contaminated and must be incorporated into the process-water system of the operation (it cannot be allowed to run into the surrounding environment).

Due to this variability in incoming density and tonnage fluctuation for other reasons, it is strongly recommended that conventional thickeners (not high-rate) be installed to provide a degree of surge and storage flexibility between the reclamation operations and the processing plant. Starting and stopping of the reclamation system is a long and complex procedure with some degree of risk (most pump/pipeline failures occur at start up) and it is inappropriate to design the system in such a way that every downstream problem interrupts the reclamation process. The thickeners also ensure a consistent feed stream in terms of volume and density to the treatment plant, which enables better process control and usually facilitates efficiency optimization. During extreme rainfall/flooding it may be necessary to pump the incoming water or thickener overflow directly to the tailings' dam for storage until the reclamation site has recovered and this facility should be incorporated into the flowsheet design in areas where high rainfall events can be anticipated.

The preferred route for the slime treatment is typically a CIL circuit. This is a result of the high-volume treatment not being suited to a pump-cell type of operation and the low grade probably not justifying the increased capital cost of a separate leach and absorption section. Also the low solution gold tenor and the possibility of *preg-robbing* by carbon species in the slime or other material absorbents is such that presentation to activated carbon as soon as possible is likely to be advantageous.

As the slime has been previously processed, gold recovery is lower than with newly mined ore and is liable to be in the range of 50–80% dissolution and adsorption of about 95%. Gold recovery is essentially from:

- the *original soluble loss* (from old filter-plant operations), which will have precipitated as a gold-cyanide species on the material surface and is now re-dissolved;

- *leachable gold* left in residue due to historical processing inefficiencies, and
- a release of *previously occluded gold* due to weathering and aging of the material.

This gold recovery will be determined during the testwork phase.

Although preg-robbing is evaluated during the testwork phase it should be appreciated that carbonaceous species present, such as old boiler ash, are not liable to be very active, may well be already loaded to their full capability with gold and will in all probability not be able to compete with the activated carbon. A leach response similar to the laboratory testwork is liable to be achieved in practice unless fine carbon has been generated during milling, for example.

Reagent consumption data will have been derived during testwork. Experience indicates that a cyanide tenor of about 60 mg/L should be maintained throughout to ensure optimum leach efficiency, although different ores may require more cyanide to drive the leach kinetics if the residence time is particularly short. Oxygen addition to every tank or alternate tanks is considered essential and should preferably maintain dissolved oxygen levels of 15–20 ppm and not less than 8 ppm. Oxygen levels higher than 20 ppm are not recommended as this may result in increased cyanide consumption. As a low leach time is the likely scenario, every effort should be made to raise the oxygen to an acceptable level at the start of leaching and this may involve injection of oxygen prior to cyanide addition. The use of oxygen to consume *cyanicides* should also be explored as a method of reducing reagent costs. For example, the conversion of ferrous species into ferric (from a cyanide consumer to a non-consumer) has proved successful although this is very pH-dependent (the optimal pH value is around 5–6) and is influenced by oxygen solubility and ferrous solubility.

Oxygen injection directly into the overland transfer pipelines can be employed to counteract cyanicides and enable the CIL leach to attain the desired oxygen in solution as quickly as possible. However, care must be exercised to ensure that the oxygen concentration at the injection point and in the pipeline does not go too high and cause accelerated corrosion when mild-steel pipelines are being used.

Leach residence time of about 7–8 h with oxygen addition is normally sufficient since the available gold is normally in a form that dissolves easily. The incremental dissolution achieved after this time is liable to be inadequate to support the capital for the equipment involved and the solution gold tenor will be so low that it will no longer provide a strong driving force to the adsorption kinetics.

A typical CIL slime circuit will comprise de-gritting via linear screens, with the de-gritted slurry being pumped to the CIL tanks. The first of the tanks could incorporate a desanding facility to prevent near-size grit build-up in the system, with re-circulation of this back to the linear screens. The linear screen oversize is re-pulped and pumped to join the CIL tailings prior to disposal to the tailings-storage facility. The CIL tanks will be mechanically agitated, incorporate an oxygen addition system and be equipped with mechanically swept screens for carbon retention. This plant section should include a slurry mass-flow calibration facility, with this being essential in a slimes circuit due to the inherent difficulty in tonnage accounting on a reclamation operation.

The leached slurry passes over linear screens to scavenge any coarse carbon escaping from the circuit and the screen undersize is pumped to the tailings disposal site. Water is recycled from the tailings-storage facility water-dams to the reclamation sites for use as monitor water.

The loaded carbon is pumped to washing screens, acid-washed to remove calcium carbonate, eluted and regenerated before being returned to the absorption circuit. Because of the potential for organic fouling of the carbon owing to rotting vegetation, historical dumping of organic waste, diesel spillage from machinery on the sites, the presence of flotation reagents and so on, it is strongly recommended that regeneration capacity employs rotary kilns that are correctly sized to ensure regeneration of all eluted carbon (*i.e.*, no bypassing).

Organic species in the slime will be absorbed on the activated carbon and organic loading on carbon can exceed 6%. While this does not appear to impair the gold-loading capability of carbon dramatically in practice, it does make it essential to thermally regenerate the carbon with every elution cycle. If this is not done, organic build-up and carbon surface coating will eventually decrease adsorption efficiency. Where flotation reagents are present they will be loaded onto the carbon and experience has shown that the resultant gases released during thermal activation can leach nickel from the kiln steel and cause premature shell failure. Rotary kilns are therefore better suited to this application as they offer rapid exhaust of internal gases.

The carbon loading is liable to be much lower than achieved in high-grade ore circuits and could be as low as 200 g/t. As a result, the eluate grade will also be low. Electrowinning from the eluate may be impractical due to competition from other metallic species. In this event, standard zinc precipitation will be the preferred final gold recovery route.

The gold recovery section of this book (Section II.5) fully covers leaching and carbon technology unit processes.

6.2. Slime treatment with pyrite recovery

If the resource material contains significant pyrite (around 0.8–1% sulfide sulfur), some of the gold is liable to be associated with the pyrite. If this pyritic gold is simply allowed to follow a slime-processing circuit as described above, it will report directly to the CIL plant where two undesirable impacts will arise. Firstly, pyrite has a high cyanide demand and will increase the overall cyanide consumption of the circuit. Secondly, gold in pyrite tends to be slow leaching and because of the short residence time available, the recovery of the pyritic gold component will be lower than that achieved for the remainder of the material (often in the range 30–35%).

Consideration must, therefore, be given to introducing a flotation process to remove the pyrite for separate treatment and this option should be evaluated during the metallurgical testwork programme (see also Chapter 14). Flotation of material of less than 0.8% sulfide sulfur is not generally viable.

The pyrite-concentrate grade that can be achieved during flotation may dictate the subsequent pyrite-processing step. If the pyrite-concentrate sulfur grade is less than 25% the pyrite can simply be cyanide leached, followed by solid/liquid separation, solution clarification and recovery of gold from solution. Leach residence time of at least 18 h will be required and cyanide consumption may be as high as 7 kg/t. Gold recovery from this processing option will typically be about 60–70%.

If the concentrate sulfur grade is at least 30% sulfur (or can be upgraded to this level), the potential of installing a pyrite burning sulfuric acid plant to roast the pyrite and generate revenue from the acid should be evaluated. The calcine (roasted pyrite) would then undergo cyanide leaching, solid/liquid separation, solution clarification and recovery of gold from solution. A leach residence time of about 18 h will be required and cyanide consumption will be lower, at about 1.5–2.0 kg/t. Gold recovery from this circuit will be in the region of 90%. These options must be evaluated during the pre-feasibility study during which an evaluation of all factors, including the sulfuric acid market, will determine any benefit from this circuit.

In both the pyrite and calcine processing circuits a carbon circuit incorporating pump cells could replace the solid/liquid separation recovery method (see Chapter 23).

In the flotation circuit, incoming slurry should pass through storage tanks to enable surge capacity, density adjustment, pH and reagent conditioning as well as to ensure that a constant volume of slime is pumped to the flotation cells to facilitate flotation optimization. The system should also incorporate a mass-flow calibration system. In the event of very low incoming density, or low sulfur levels, a facility to bypass the feed to the CIL feed thickeners should exist.

The flotation tails would report to the CIL feed thickeners with the underflow being directed to the CIL plant and the overflow water being recycled to the reclamation system.

6.3. Sand treatment

Obviously the major difference between sand and slime is the coarser particle size of sand. As previously noted, up to about 10% sand can be *carried* by slime and tolerated in the circuit. Sand percentages above this will cause accelerated erosion of mild-steel pipes and valves, and the grit will settle out of suspension in the CIL tanks, resulting in reduced residence time due to volume loss (grit build-up) in the CIL tanks, as well as the necessity to take tanks out of circuit for de-gritting.

It follows therefore that the sand must be milled to enable subsequent processing. Milling to about 45–55% passing 74 μm is usually adequate to overcome the erosion and settling problems. The extent of milling to be used (*i.e.*, to what degree of fineness) will be dictated by mill throughput rates for the various degrees of fineness and the incremental change in recovery that can be achieved at these different grind levels. Considering the relatively low head-grade of most sand deposits and the fact that milling is a costly process, testwork must establish at which point finer grinding does not produce any additional economic benefit. Typically, recovery will improve with finer grind, but the reduction in throughput or increase in cost required to achieve this may not be justified by the small incremental gold-recovery benefit.

Following size reduction, the processing of the sand will be the same as outlined for slime and the same considerations related to flotation should be applied to sulfur-bearing sand.

7. ENVIRONMENTAL REHABILITATION

The objective of conducting environmental rehabilitation is to ensure that all environmental aspects required for eventual mine closure or to minimize ongoing environmental liabilities are adequately addressed before reclamation activities on a site are completed.

An environmental impact assessment must be undertaken to ensure that all environmental impacts arising from the reclamation, processing and re-deposition activities are taken into consideration. Agreement will normally be required from the relevant authorities prior to the project proceeding to implementation and in this respect they will require guarantees that environmental impacts are kept at a minimum and that all closure obligations and liabilities are clearly understood and funded. The use of external independent consultants is advisable and ensures an unbiased input to the assessment process.

For completed reclamation sites it is vitally important to understand what constitutes acceptable closure standards. These have tended to become more rigorous with the passage of time and it is now generally accepted that minimum standards entail cleaning down to ground level, conducting soil amelioration and planting grass. When these activities have been completed, vegetation established and run-off water meets acceptable standards, formal closure may be obtained.

Disposal and dumping of untreated material such as screen oversize and physical contaminants need to be fully addressed through on-site rehabilitation in conjunction with the relevant authorities.

The handling of radiation or contamination from other problematic species such as cadmium, copper or zinc needs to be identified at an early stage and an action plan to deal with this problem prepared for approval by the relevant authorities.

The cost, complexity and impact on production of final environmental cleanup of remnant material on sites should not be underestimated.

8. PROCESS FLOWSHEETS

Simplified flowsheets for slimes reclamation (Fig. 7), sand reclamation and milling (Fig. 8) and residue treatment (Fig. 9) are presented below.

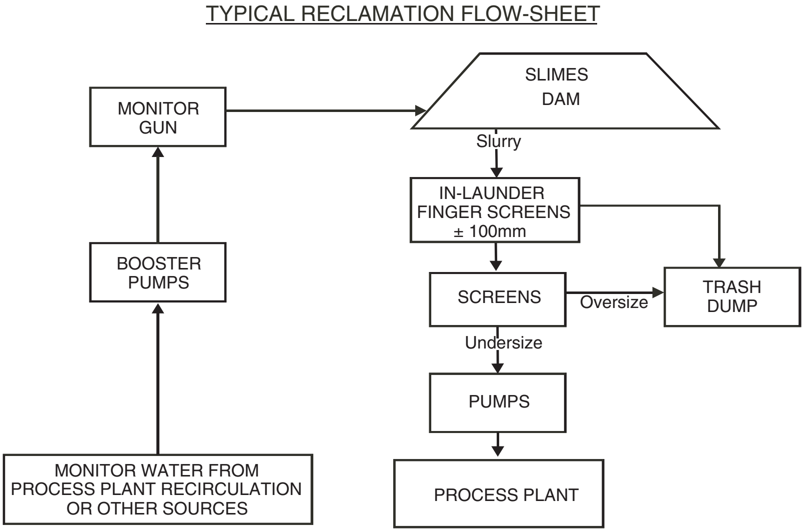

Fig. 7. Simplified flowsheet for slimes reclamation.

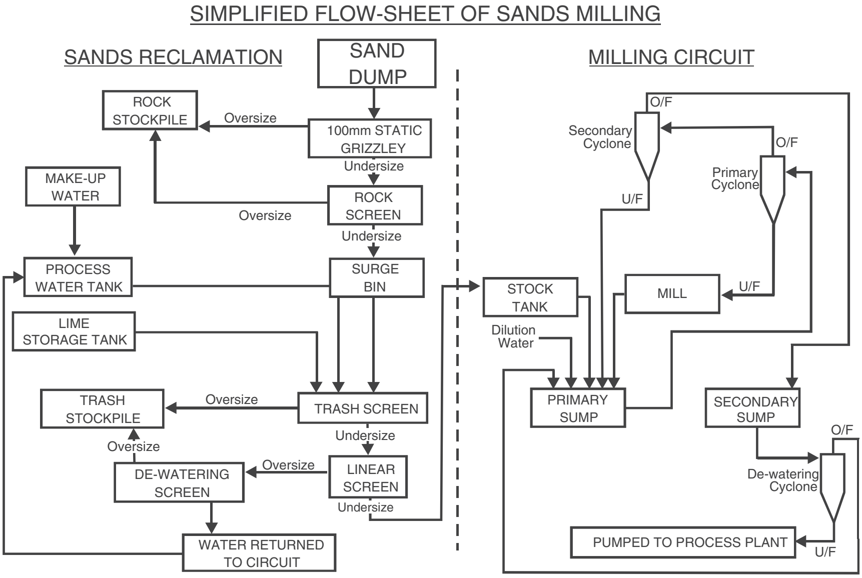

Fig. 8. Simplified flowsheet for sand reclamation and milling.

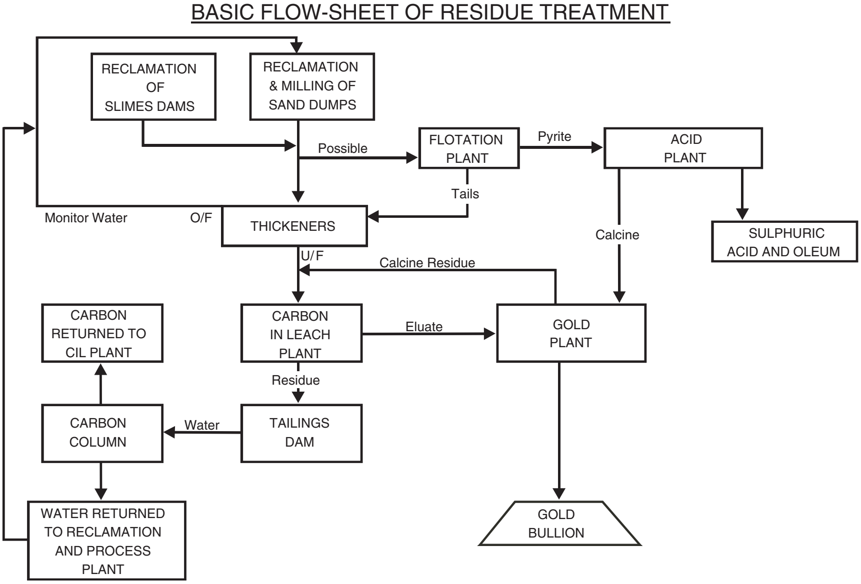

Fig. 9. Simplified flowsheet for residue retreatment.

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Further Reading

Stanley, G.G. 1987. The Extractive Metallurgy of Gold in South Africa, S.A.I.M.M. Monograph series M7. South African Institute of Mining and Metallurgy, Johannesburg (Chapter 12).

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Con is a registered Certificated Engineer with the Engineering Council of South Africa and is a member of the Association of Mine Resident Engineers.

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PART III CASE STUDY FLOWSHEETS

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Chapter 32

Gold-copper ores

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The association of gold and copper mineralization in commercially viable ore is a common occurrence. At one end of the spectrum is the predominantly copper ore, which contains levels of gold mineralization. This would be uneconomic to mine for its gold content, but the gold provides a significant opportunity value. The gold is recovered with the copper and is eventually recovered from the residues of copper refining. The development of processes for dealing with such ore is discussed in Chapter 33.

This chapter deals with the other end of the spectrum, where copper is present at nuisance levels, which adds to the cost of treating the ore, but generally does not provide additional income. The chapter reviews recent and emerging developments in processes targeted at minimizing the cost impact of the copper, which may be manifested in poor gold recovery, high cyanide consumption and high carbon-management and bullion-refining costs.

1. CHEMISTRY OF COPPER CYANIDES

A brief review of the reactions that occur between cyanide and most copper minerals will illustrate how cyanide is consumed and where it is irretrievably lost and sets the background to the various processes that have been developed to address the problems posed by copper in gold ores.

Most copper minerals react readily with cyanide (Hedley and Tabachnick, 1958; Staunton, 1991; Adams, 1999). The solubility of the major copper minerals is given later (Table 1) (Hedley and Tabachnick, 1958; Lower and Booth, 1965). Copper can form four complexes with up to four cyanide

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Table 1
Solubility of copper minerals in 0.1% NaCN solutions

Mineral	Formula	Percent total copper dissolved[a]		g NaCN/g Cu[b]	Extraction (% Cu)[b]
		23°C	45°C		
Azurite	$2Cu(CO)_3 \cdot Cu(OH)_2$	94.5	100.0	3.62	91.8
Malachite	$2CuCO_3(OH)_2$	90.2	100.0	4.48	99.7
Chalcocite	Cu_2S	90.2	100.0	2.76	92.6
Covellite	CuS	—	—	5.15	95.6
Native copper	Cu	90.0	100.0	—	—
Cuprite	Cu_2O	85.5	100.0	4.94	96.6
Bornite	$FeS \cdot 2Cu_2S \cdot CuS$	70.0	100.0	5.13	96.0
Enargite	Cu_3AsS_4	65.8	75.1	—	—
Tetrahedrite	$(Cu,Fe,Ag,Zn)_{12}Sb_4S_{13}$	21.9	43.7	—	—
Chrysocolla	$CuSiO_3 \cdot nH_2O$	11.8	15.7	—	—
Chalcopyrite	$CuFeS_2$	5.6	8.2	2.79	5.8

[a] Data after Hedley and Tabachnick (1958).

[b] Data after Lower and Booth (1965). Cyanide consumption is expressed as g. NaCN/g of contained copper, data being generated by leaching at room temperature for 6 h.

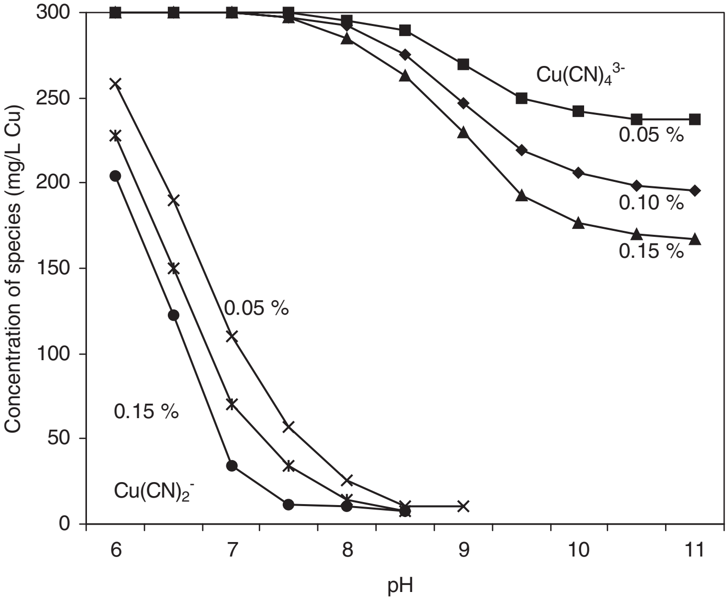

Fig. 1. Distribution of Cu–CN complexes as a function of pH and NaCN concentration (after Wang and Forssberg, 1990).

ligands. The range of cyano complexes depends on conditions such as cyanide concentration and pH, as shown in Fig. 1.

1.1. Copper–cyanide complexes

Although copper (II) cyano complexes have been characterized, they are unstable and decompose rapidly forming copper (I) complexes and cyanate, OCN^-. Therefore, the presence of cupric copper in an ore will result in the loss of cyanide as cyanate.

When aqueous solutions of copper sulfate and sodium cyanide are mixed in stoichiometric proportions, greenish-yellow cupric cyanide is precipitated according to the following series of reactions:

$$CuSO_4 + 2NaCN \rightarrow Cu(CN)_2 + Na_2SO_4 \tag{1}$$

then on standing or heating:

$$2Cu(CN)_2 \rightarrow 2CuCN + (CN)_2 \tag{2}$$

and

$$(CN)_2 + 2OH^- \rightarrow CNO^- + CN^- + H_2O \tag{3}$$

then in excess cyanide:

$$CuCN + xNaCN \rightarrow Na_xCu(CN)_{x+1} \tag{4}$$

where $x = 1$, 2 or 3.

The copper (I) complexes that are formed are moderately stable complexes. When copper (I) minerals are leached in cyanide, neither cyanogen nor cyanate is formed.

The compound $NaCu(CN)_2$ is only slightly soluble in water, tending to break down into CuCN, which is precipitated, and a higher complex in the series:

$$2NaCu(CN)_2 \rightarrow CuCN(\downarrow) + Na_2Cu(CN)_3 \tag{5}$$

The cyanogen formed according to Eq. (2) is a highly poisonous but also highly water-soluble gas and it reacts with alkali to form cyanide and cyanate.

Both the cyanide concentration employed and the ionic strength and composition of the solution can influence the equilibrium mixture of copper complexes formed. Higher free-cyanide levels will favour the higher-order species.

As the pH value of the solution also determines the concentration of the free cyanide present via the equilibrium shown in Eq. (6), it is also a significant factor in determining the predominant copper species in solution:

$$CN^- + H^+ \rightarrow HCN \tag{6}$$

The Eh–pH diagram for the copper–cyanide–water system given in Fig. 2 is representative of conditions typically found in copper–gold plants in which

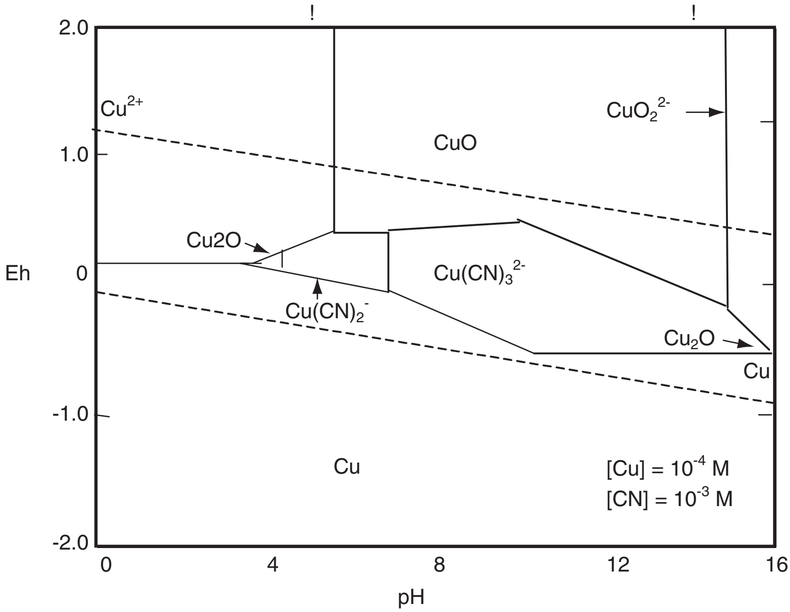

Fig. 2. Eh-pH diagram for the Cu–CN–H_2O system (CuCN is ignored; after Osseo–As are et al., 1984).

some free cyanide exists. The copper and cyanide concentrations impact on the stability regions shown in this figure.

From the above diagram it can be seen that the most common cyanide species present under typical leaching conditions is $Cu(CN)_3^{2-}$. Thus, if copper is not removed from the leach circuit, natural degradation at the tailing dam will deplete free and weakly bound cyanide so that $Cu(CN)_2^-$ in recycled tailings water will react with more free cyanide in the leach liquor to form $Cu(CN)_3^{2-}$ and $Cu(CN)_4^{3-}$.

In the presence of hypersaline waters, it has been shown by Lukey *et al.* (1999) that the predominant species is typically $Cu(CN)_4^{3-}$. Thus, depending upon the free-cyanide concentration, the chloride ion concentration and the solution pH value, all or any of the following species may be present in equilibrium, $Cu(CN)_2^-$, $Cu(CN)_3^{2-}$ and $Cu(CN)_4^{3-}$.

Fig. 1 plots the distribution of the various species as a function of pH and sodium cyanide concentration and shows that high pH and free-cyanide conditions (low HCN) favour the formation of the higher-order copper (I) complexes (Wang and Forssberg, 1990). This figure also illustrates that for any given conditions usually only two of the species are present in any significant quantities. By determining the particular copper species present, cyanide concentration and pH have a significant influence on the rate of adsorption of copper onto carbon and the equilibrium loading capacity of the carbon for copper, as shown in Fig. 3. The formation of $Cu(CN)_2^-$ is favoured at pH values below 6 and at very low cyanide concentrations, whereas the $Cu(CN)_4^{3-}$ species is favoured at high pH and high cyanide concentrations and in hypersaline solutions (bearing in mind that high pH conditions are impractical when operating with hypersaline water).

The lower adsorption of $Cu(CN)_4^{3-}$ on to activated carbon accounts for the use of high cyanide concentrations to improve the selectivity of gold over copper when this adsorbent is employed for gold recovery and the use of low cyanide concentrations to promote selectivity and higher adsorption of $Cu(CN)_3^{2-}$ on to activated carbon as a copper removal process using activated carbon (Sceresini and Staunton, 1991).

Copper–cyanide complexes have limited ability to leach gold; thus the free-cyanide concentration in solution must be maintained at a level that ensures maximum gold dissolution. This is a problem when using hypersaline process water owing to the upper limit on pH value because of the buffering effect of the high magnesium content.

An indication of the relative proportions of the different species present in solution can be obtained by measurement of the molar ratio of sodium cyanide to copper in solution. Typically, this ratio varies between 2.5 and 3.5, although a number of operations are known to favour a ratio of CN/Cu of greater than 4.5:1 (Jay, 2000).

1.2. Solubility of copper minerals in cyanide solutions

Hedley and Tabachnick (1958) conducted leaching tests on copper minerals under the following conditions:

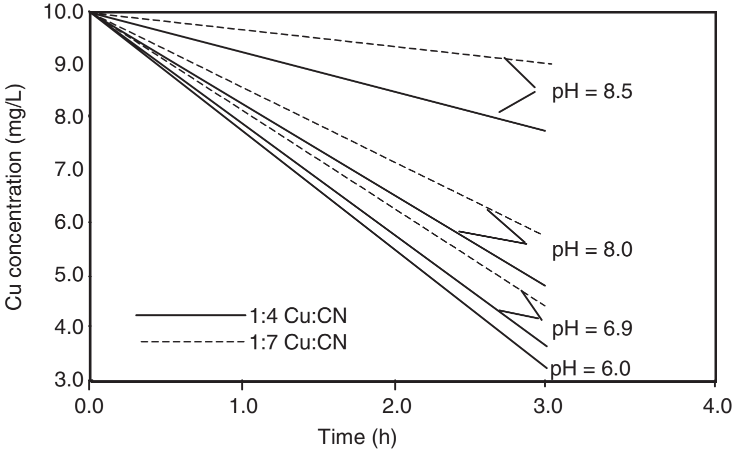

Fig. 3. Effect of pH and cyanide concentration on copper loading rate.

Mineral particle size −100 mesh (150 μm)
Copper in mineral 0.183–0.267%
NaCN concentration 0.10% initial
Solution:ore ratio 10:1
Reaction time: 24 h

The results are listed in Table 1.

1.3. Reactions of copper minerals in cyanide solutions

The cyanidation of copper–gold ores containing the common oxide and secondary sulfide copper minerals results in irreversible cyanide loss to CNO^- and SCN^- and copper solubilization as cuprous cyanide complexes.

Some of the possible reactions are shown below:

$$Cu_2O + 6NaCN + H_2O \rightarrow 2Na_2Cu(CN)_3 + 2NaOH \tag{7}$$

$$Cu_2S + 7NaCN + \tfrac{1}{2}O_2 + H_2O \rightarrow 2Na_2Cu(CN)_3 + 2NaOH + NaCNS \tag{8}$$

$$2CuO + 7NaCN + H_2O \rightarrow 2Na_2Cu(CN)_3 + 2NaOH + NaCNO \tag{9}$$

$$2CuS + 8NaCN + \tfrac{1}{2}O_2 + H_2O \rightarrow 2Na_2Cu(CN)_3 + 2NaOH + 2NaCNS \tag{10}$$

The cyanidation of Cu(II) minerals with the consequent formation of cyanogen, $(CN)_2$, results in the loss of cyanide in the proportion of 0.5 mol of cyanide per mole of Cu(II) leached, *i.e.*, 0.39 kg NaCN/kg Cu(II). Cupric cyanogen complexes are first formed, then breaking down to the cuprous form and liberating cyanogen, which in turn reacts with alkali to form cyanide and cyanate.

For example, in the cyanidation of malachite and azurite minerals, the copper carbonate component leaches as follows:

$$2CuCO_3 + 8NaCN \rightarrow 2Na_2Cu(CN)_3 + 2Na_2CO_3 + (CN)_2 \tag{11}$$

then

$$(CN)_2 + 2NaOH \rightarrow NaCNO + NaCN + H_2O \tag{12}$$

The overall reaction is

$$\begin{aligned} &2CuCO_3 + 7NaCN + 2NaOH \\ &\rightarrow 2Na_2Cu(CN)_3 + 2Na_2CO_3 + NaCNO + H_2O \end{aligned} \tag{13}$$

With sulfide minerals, some thiocyanate is formed. This reaction becomes more important at temperatures above 35°C and there is also evidence that the addition of a lead salt increases the formation of thiocyanate, as discussed later.

While only cupric oxides result in the irreversible loss of cyanide as cyanate, both mono and divalent copper sulfide minerals result in the loss of cyanide as thiocyanate. While this reaction can be reversed, recovery methods based on oxidation with ozone or hydrogen peroxide are chemically feasible, but no commercial application has yet been applied.

1.4. Dissolution of gold and copper in cyanide solutions

The dissolution of both gold and copper in aerated cyanide solutions has been shown to be dependent on both the oxygen and the cyanide concentrations. It has further been shown that in aerated solutions, the dissolution of gold is controlled by cyanide diffusion at cyanide concentrations below about 2 mM, and by oxygen diffusion at cyanide concentrations above this (Habashi, 1967).

Copper dissolution is similarly controlled by cyanide diffusion at cyanide concentrations below about 1 mM, and by oxygen diffusion at cyanide concentrations above 6 mM (Drok and Ritchie, 1997).

1.5. Preg-robbing of gold onto copper and copper minerals

Under cyanide-deficient conditions, Adams *et al.* (1996) reported that gold will react with copper minerals and is therefore lost to tailings. They proposed the following reactions:

$$\mathrm{Cu(OH)_2 + Au(CN)_2^- + e \rightarrow AuCN \cdot CuCN(\downarrow) + 2OH^-} \tag{14}$$

$$\mathrm{AuCN \cdot CuCN + e \rightarrow Au^o + Cu(CN)_2^-} \tag{15}$$

These reactions may be driven by oxidation of the copper mineral surfaces. The reaction was reported to proceed more rapidly with the more reactive copper minerals, such as native copper, chalcocite and covellite.

Nguyen *et al.* (1997) reported that the rate of cementation of the gold onto native copper increased with the amount of native copper present. Moreover, cemented gold did not fully redissolve until all the metallic copper had dissolved in the cyanide solution. At low initial cyanide concentrations (50–500 mg/L NaCN), the level of free cyanide in solution rapidly decreases to 5–20 mg/L, resulting in a lack of free cyanide for the subsequent gold cementation, gold redissolution and copper dissolution. The dissolution of copper increased with an increase in the initial cyanide concentration. Furthermore, the dissolution of copper is incomplete unless the initial concentration of NaCN is greater than 1,000 mg/L, and thus, after gold is cemented onto copper, it cannot redissolve completely unless all of the copper first dissolves under conditions in which an excess of free cyanide exists.

Quach *et al.* (1993) observed that chalcopyrite adsorbs gold cyanide almost quantitatively. The experiments were conducted at 30°C at a pH value of 11 and with no excess cyanide present. The redox potential of the solution dropped rapidly during the experimental runs.

Rees and van Deventer (2000) examined the ability of pyrite and chalcopyrite to adsorb gold from cyanide-deficient solutions with and without activated carbon. Chalcopyrite was found to be very strongly preg-robbing and competed with activated carbon to remove the majority of gold from solution. Pyrite was also strongly preg-robbing and, in cyanide-deficient solutions adsorbed the majority of the gold in preference to the carbon. The degree of adsorption onto the ore or activated carbon was a function of the kinetics of the adsorption process.

The role of the cyanide complexes of copper, silver, zinc, nickel and iron was also examined. It was found that these complexes countered preg-robbing and serve to stabilize the aurocyanide complex by precipitating prior to gold precipitation. When cyanide or cyanide species were present in solution, the adsorption onto activated carbon was found, in general, to take preference to the adsorption onto the minerals. The ability of the sulfide ore to adsorb $Au(CN)_2^-$ was found to be a function of how rapidly the ore consumed cyanide and precipitated metal–cyanide complexes.

Rees and van Deventer proposed a mechanism whereby the gold is reduced at the chalcopyrite surface through the formation of an adsorbed intermediate, similar to that proposed by Adams *et al.* (1996). The gold was reduced, along with the oxidation of the chalcopyrite to form copper–cyanide complexes in solution. Reduction of gold on the pyrite was observed to occur with the release of zinc as an impurity into solution.

1.6. Effect of copper–cyanide complexes on the gold cyanidation process

As molar ratio of 4:1 cyanide to copper is required to maintain acceptable gold cyanidation rates, this is typically taken into consideration during the ore-testing phase. However, significantly higher cyanide consumption can occur in practice than is expected on the *prima facie* cyanide-soluble copper content, due to the recycling of copper with tailing dam return water. The bulk of the copper exiting the plant in the tailing solution is present as the $Cu(CN)_3^{2-}$ and $Cu(CN)_4^{3-}$ complexes, while the tailings return water has a preponderance of the lower cyanide complex, $Cu(CN)_2^-$, owing to the atmospheric decomposition of free and weakly-bound cyanide. Therefore, additional cyanide is consumed by the $Cu(CN)_2^-$ complex in the return water, which acquires a further 1–2 mol of cyanide from the process and promptly transports this additional cyanide to the tailings dam.

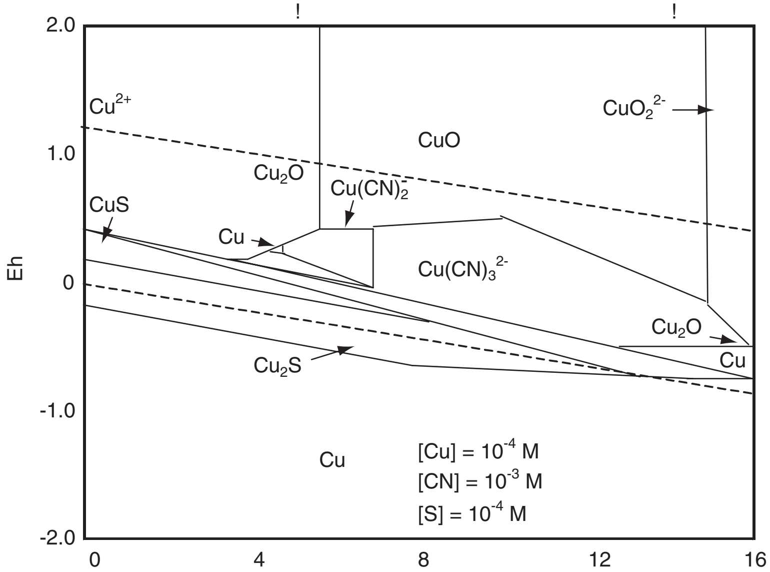

Fig. 4. Eh-pH diagram for the Cu–CN–S–H_2O system at 25°C (after Osseo-Asare *et al.*, 1984).

1.7. Effect of sulfides with copper on the gold cyanidation process

The presence of sulfides in the ore can also have a significant impact on cyanidation of gold/copper ores. Fig. 4 shows the Eh–pH diagram for the system.

Intense aeration and preferably oxygen gas injection is required to optimize leaching efficiency in the presence of sulfides. Prior to cyanidation with gaseous oxygen injection becoming prevalent, the addition of leach-promoting cations such as lead salts (*e.g.*, lead nitrate or litharge) showed significant benefits by acting to depolarize the gold surface and prevent passivation by sulfide film formation (Habashi, 1967). Kudryk and Kellogg (1954) concluded that even at trace levels, sulfide poisons the gold surface toward the cathodic reduction of oxygen, but does not affect the anodic reaction. This also appears to be the case when ammonia/cyanide leaching is practised.

The passivating effect of sulfide and the benefit of lead addition has been demonstrated during a test program to determine the potential benefit of the Sceresini copper/cyanide recovery process (Sceresini and Richardson, 1991). A series of four samples with increasing copper content was tested. The ore contained native copper, oxide copper and chalcocite. The cyanidation test program was designed to compare the relative merits of ammoniacal cyanidation in the presence of the copper–gold ore with the (simulated) effect of copper removal by adsorption onto activated carbon. Sufficient cyanide was added to maintain a 4:1 mole ratio of CN/Cu.

The ammoniacal leach test samples were bottle-rolled for 32 h and the straight cyanide tests were bottle-rolled over two 24-h stages with filtration and washing of the first-stage leach residue followed by repulping with fresh cyanide solution and leaching for a further 24 h. The overall gold extraction decreased progressively with increasing copper content, but surprisingly the higher copper samples showed little benefit from the second leaching stage.

In each series, gold extraction dropped as thiocyanate production increased. This indicated that an increasing amount of sulfide ion was liberated as the chalcocite content increased. It had been expected that the second-stage leach using fresh cyanide solution would yield high gold extraction, but it would appear that a sulfide film had formed on the gold surface during the first-stage leach and that this film was not removed by washing of the filter cake. The cyanidation tests that were conducted using the ammonia–cyanide leach technique gave similar results.

The series of tests were repeated using new samples, which were cyanided for 24 h only, but with the addition of 250 g/t of lead nitrate. A parallel ammonia–cyanide leach of the samples was again carried out with 250 g/t of lead nitrate. All of the previous cyanidation residues were also re-leached with 250 g/t lead nitrate addition. The effect of the lead salt was to increase gold extraction from all samples, including the previous cyanidation residues both with and without ammonia, to approximately 95%.

The test data are shown in Table 2.

The re-leach residues with 250 g/t of lead nitrate resulted in high gold extractions, with the final residues assaying 0.127, 0.149 and 0.121 g/t. On the other hand, the ammoniacal re-leach residues assayed 1.380, 1.080 and 0.275 g/t.

Tables 3 and 4 show the results of comparison of ammoniacal cyanidation with and without lead nitrate of 250 g/t lead nitrate addition after 32 h of cyanidation.

2. GOLD RECOVERY

The presence of cyanide-soluble copper affects gold recovery from the cyanide solution. The carbon-adsorption process has a degree of tolerance to copper in ores as discussed below and this process has largely overtaken the traditional gold cementation processes such as the Merrill–Crowe process, not because of greater tolerance to copper in pregnant solution, but because of the inherent advantages of the carbon-in-pulp (CIP)/carbon-in-leach (CIL) process over the traditional leach-filtration–clarification–deaeration–precipitation process.

Table 2
Effect of Pb^{2+} in cyanidation of a copper–gold ore

Sample	CN Sol. Cu (g/t) (estimated) extracted	CN added (kg/t)		Gold extracted (%)			SCN^- (mg/L)	OCN^- (mg/L)	NaCN consumed (kg/t)
		Stage 1	Stage 2	Stage 1	Stage 2	Overall	Stage 1	Stage 1	
1	(180) *173*	1.25	1.15	83.57	13.56	97.13	2.78	68.9	1.55
2	(600) *825*	1.68	1.27	45.13	24.71	69.84	45.7	36.5	2.63
3	1,260 *1,470*	1.63	1.29	41.20	32.58	73.78	156	33.3	2.58
4	3,680 *4,245*	8.21	1.24	23.29	21.08	44.37	577	45.4	9.28
Repeat 1-stage cyanidation of samples 2, 3 and 4 with 250 g/t lead nitrate									
2	(600) *633*	2.25	—	98.05	—	98.05	79.1	—	1.73
3	(1,260) *1,200*	3.25	—	93.46	—	93.46	188	—	2.65
4	(3,680) *4,350*	12.5	—	91.41	—	91.41	1060	—	10.32
Re-cyanidation of Stage 2 leach residues with 250 g/t lead nitrate									
2	80[a]	2.00	—	92.60[b]	—	95.45[c]	No assay	No assay	0.65
3	126[a]	2.00	—	73.81[b]	—	95.34[c]	—	—	0.87
4	647[a]	2.00	—	92.10[b]		96.10[c]	—	—	1.5

[a] Copper (g/t) extracted from the initial two-stage cyanidation.
[b] Percent gold extracted from the initial two-stage cyanidation.
[c] Calculated percent gold extracted based on the initial two-stage cyanidation head grade.
All samples were cyanided for 24 h.

Table 3
Effect of Pb^{++} in ammoniacal cyanidation of a copper–gold ore

Sample	CN sol. Cu (g/t)	Ammonia (kg/t)	NaCN (kg/t)	Gold extracted (%)	SCN$^-$ (mg/L)	OCN$^-$ (mg/L)	NaCN consumed (kg/t)
2	600	1.51	2.5	51.49	No assay	No assay	1.99
3	1,260	1.51	2.5	29.20	No assay	No assay	2.31
4	3,680	1.51	2.5	79.40	No assay	No assay	2.40
Repeat ammoniacal cyanidation with 250 g/t lead nitrate							
2	600	1.51	2.5	87.43	No assay	No assay	1.83
3	1,260	1.51	2.5	51.58	No assay	No assay	2.29
4	3,680	1.51	2.5	86.01	No assay	No assay	2.46

Note. Sample 2: residue assay without lead, 1.300 g/t, residue assay with lead, 0.235 g/t. Sample 3: residue assay without lead, 1.600 g/t, residue assay with lead, 1.070 g/t. Sample 4: residue assay without lead, 0.498 g/t, residue assay with lead, 0.288 g/t.

Table 4
Comparison of copper extraction with ammoniacal and straight cyanidation with 250 g/t lead nitrate

Sample	CN sol. Cu (g/t)	Copper extraction (mg/L)		Gold extracted (%)		Cyanide consumed (kg/t)	
		Ammoniacal cyanide	Cyanide	Ammoniacal cyanide	Cyanide	Ammoniacal cyanide	Cyanide
2	600	468	422	87.43	98.05	1.83	1.73
3	1,260	770	800	51.58	93.46	2.29	2.65
4	3,680	630	2,900	86.01	91.41	2.46	10.32

2.1. Merrill–Crowe process

In the Merrill–Crowe process, the copper is precipitated along with gold and silver, resulting in a higher consumption of zinc dust. The copper must also be separated from the gold by digesting the precipitated gold slimes in sulfuric acid prior to smelting. This is a costly and time-consuming practice and produces an acidic copper sulfate solution that must undergo further processing before disposal. Cementation of copper using scrap iron is practiced when the quantity of copper makes recovery worthwhile. The process is discussed in detail in Chapter 24.

2.2. Carbon-in-pulp and Carbon-in-leach process

Under certain conditions, copper will readily adsorb onto activated carbon and displaces gold, thereby necessitating a higher carbon inventory and accelerated elution rates in order to maintain high gold and silver recovery.

The copper adsorption kinetics and the equilibrium loading are both sensitive to the particular copper species in solution. Conditions which result in the formation of $Cu(CN)_3^{2-}$ and $Cu(CN)_4^{3-}$, high pH value and high-free-cyanide concentrations, will stabilize the copper in solution with resultant lower levels of copper on the carbon. Conversely, copper loading is enhanced at low pH values and low-free-cyanide concentrations, with $Cu(CN)_2^-$ the predominant species in solution. This relationship is exploited in the Sceresini copper/cyanide recovery process (Sceresini and Staunton, 1991). The higher CN/Cu mole ratio that is required for good leach performance is also beneficial in minimizing the amount of copper adsorbed by activated carbon.

While this is the norm for the operation of cyanidation circuits, operating at pH values over 10 is impractical when the process water is hypersaline, owing to the high alkali consumption cost incurred due to the buffering effect of magnesium precipitation, which commences at about pH 9.3. This is the dilemma facing operations that do not have access to low-salinity water supplies and copper contamination in these circumstances poses serious problems.

Whenever severe copper contamination of the carbon occurs it is necessary to include a cold cyanide-elution step to strip the copper prior to hot elution of the gold and silver. Failure to do so will result in the copper being deposited along with gold and silver at the cathode and production of high-copper gold bullion. Very little gold is eluted at ambient temperature (Sceresini and Richardson, 1991).

Copper is not removed from loaded carbon by acid washing with hydrochloric acid, either hot or cold, but commercial-grade nitric acid, diluted with water on a one-to-one basis and heated to 90°C will elute the copper, but will also strip a significant quantity of gold.

3. PROCESSES FOR TREATING HIGH-COPPER GOLD ORES

As shown in Table 1, many copper minerals are readily leached by cyanide. Each 1% of reactive copper will consume about 30 kg/t of cyanide (Drok and Ritchie, 1997), but the Lower and Booth (1970) data show that ores that contain copper sulfide minerals will consume significantly greater amounts of cyanide – up to 51.5 kg/t per 1% of reactive copper for covellite, due to the formation of thiocyanate and cyanate in addition to copper cyanide.

A number of cyanide-based processes have been examined for the treatment of copper–gold ores. Research has focussed either on the removal of copper before cyanidation or the prevention and/or minimization of the impact of copper on reagent consumption and gold recovery. Treatment options include bulk flotation of copper-rich sulfide ores; selective copper flotation;

acidic, alkaline or ferric ion leaching; and ammonia pre-leaching of the ore prior to conventional cyanidation.

In addition, alternative lixiviants such as thiourea, chlorine, bromine, iodine and thiosulfate have also been investigated (Avraamides, 1982); these are covered in Chapters 21 and 22.

A number of processes that address the treatment of high-copper leach solutions, either before or after gold recovery, have been developed. These processes have focussed on recovering the copper and cyanide with the value of the recycled cyanide and the possible sale of the copper off-setting the recovery process costs, and include the Sceresini process, which selectively removes the majority of the copper prior to completion of the dissolution and adsorption of the gold and a raft of other processes that are applied to the recovery of the copper cyanides after gold recovery. These processes include Cutech, Metallgesellschaft Natural Resources (MNR), sulfidization–acidification–recycling–thickening (SART), Cyanomet, Augment, Vitrokele, University of British Columbia (UBC) solvent extraction (SX), Hannah, Oretek CPC and Cyanisorb, although the latter is specifically targeted to recovering WAD and free cyanide from tailings slurry, but does not recover any copper, which is precipitated as cuprocyanide.

The copper/cyanide recovery processes are discussed in Section 4. These processes utilize cyanidation conditions that maximize gold and silver recovery by maintaining optimal CN/Cu molar ratio and solution pH value >10 to address the subsequent recovery of the cyanide and the copper from the cyanidation tailings and were developed in countries that had low-salinity water supplies. The Sceresini process on the other hand is a two-stage process that utilizes the lower pH limitations of hypersaline water to enhance copper adsorption, with copper being removed in the first stage, thereby allowing optimal cyanide concentration for maximum gold extraction and adsorption after copper recovery. The Oretek CPC process (Jay, 2000, 2001) has the potential to be a two-stage process if a solid-polymer bead can be produced commercially. The resin would be applicable at higher pH values than the carbon, which requires lower pH for copper selectivity over gold.

3.1. Use of ammonia for minimization of the effect of copper

One of the methods that has elicited much research has been the “selective” leaching of gold by an ammoniacal-cyanide solution. The effect of ammoniacal cyanidation of gold–copper ore as a means of reducing the effect of copper has been known for over 100 years (Hunt, 1901), where ammonium chloride with lime was used to suppress copper interference. It has been found that the addition of 1–2 g/L ammonia to a standard cyanide leach solution can improve the apparent “leach selectivity” for gold over copper.

Many papers have been published on the effect of ammonia with cyanide for the treatment of copper–gold ores and several mechanisms have been proposed for this system. It is generally believed that the effect of ammonia addition on gold leaching in cyanide solutions falls into one or more of the following categories (Jeffrey *et al.*, 2002):

1. *Complexation of copper* (*I*). Since it is known that ammonia can complex with copper (I), it has been proposed that mixed copper-ammonia-cyanide complexes are formed in the leaching solutions (Muir *et al.*, 1991, 1993). These complexes are then able to react with gold, providing a source of the cyanide ion, CN^-.
2. *Formation of an additional oxidant, copper* (*II*). In the presence of oxygen, copper (I) ammine complexes are rapidly oxidized to copper (II), which can act as an additional oxidant for gold leaching (Xu *et al.*, 1992; Muir *et al.*, 1993; Hayes and Corrans, 1992). Oxygen is particularly inefficient in highly saline solutions, as its solubility is limited. The presence of copper (II) has the potential to substantially increase the dissolution rate of gold.
3. *Precipitation of copper*. It has been suggested that the main role of ammonia in the ammonia–cyanide leach system is to promote the precipitation of copper (Muir *et al.*, 1993; Deng and Muir, 1994; La Brooy, 1992; Drok and Ritchie, 1997). Dawson *et al.* (1997) have suggested that a mixed ammonia–cyanide solid, $Cu_3(NH_3)_3(CN)_4$, is formed during leaching of copper minerals in the ammonia–cyanide system.

Costello (1991) and Hayes and Corrans (1992) proposed another mechanism where a mixed complex such as $Cu(NH_3)_2(CN)_2$ is responsible for gold leaching, perhaps anaerobically.

Drok and Ritchie (1997) carried out an investigation of the selective leaching of gold over copper using ammoniacal cyanide. All tests were carried out at a cyanide concentration of 32 mM, which is well into the oxygen-diffusion-controlled region for the leaching of both copper and gold. In the absence of ammonia and under conditions of oxygen-diffusion control, the leach rates of copper and gold in cyanide are not the same. This is apparently because of a difference in oxygen-reduction mechanism on the differing metal surface. Oxygen is reduced in a four-electron process to hydroxide on copper (Eq. (16)), whereas oxygen is reduced predominantly via a two-electron process to hydrogen peroxide on gold (Eq. (17)):

$$4Cu + O_2 + 8CN^- + 2H_2O \rightarrow 4Cu(CN)_2^- + 4OH^- \tag{16}$$

$$2Au + O_2 + 4CN^- + 2H_2O \rightarrow 2Au(CN)_2^- + H_2O_2 + 2OH^- \tag{17}$$

For this reason alone, copper leaching in aerated solutions is faster than gold leaching in identical solutions. At low copper (I) concentrations, both gold and copper dissolution occurs at rates comparable to that in the absence of copper (I). This finding concurs with plant observations as well as the cyanidation result for Sample 1 compared with Samples 2, 3 and 4, in Table 2. It was also found that over the range of copper (I) concentrations investigated (covering the entire copper solubility range), copper always leached faster than gold and is probably due to the difference in oxygen-reduction mechanism on gold and copper.

Drok and Ritchie (1997) prepared the gold samples by plating from a solution dosed with silver nitrate, which resulted in a gold–silver alloy (~0.7% Ag), to more closely mimic naturally occurring gold, while other researchers (Zheng *et al.*, 1995) used pure metallic gold in their experiments. When ammonia was added to the cyanide solution, there was only a slight decrease in the leaching rate of the gold–silver alloy, but with almost pure gold as used by Zheng, the gold leach rate was found to decrease as the ammonia concentration was increased. Drok and Ritchie (1997) also found that the dissolution rate of copper in cyanide showed a slight decrease with increasing ammonia concentration, but the copper leached faster than gold over the entire range of ammonia concentrations studied, representing an ammonia/cyanide ratio from 0 up to 2.5.

Drok and Ritchie also briefly studied the electrochemistry of this system and found from the shape of the gold-oxidation polarization curves that ammonia strongly passivates gold oxidation, but not in the potential region where leaching occurs in aerated cyanide solutions. The polarization curves published by Zheng *et al.* (1995) showed that ammonia largely suppresses the anodic polarization curve for 'pure' gold.

When gold was cyanided in the presence of copper (I), the leach rate for both the gold and the copper was lowered as the copper concentration increased, owing to depletion of free cyanide, but the copper leach rate started to decrease at a lower copper (I) concentration than did the gold. While copper can only dissolve by the action of oxygen, gold can dissolve either as the result of oxygen reduction (to peroxide or hydroxide) or as a consequence of copper (I) cementation:

$$\mathrm{Au^o + Cu(CN)_2^- \rightarrow Au(CN)_2^- + Cu^o} \tag{18}$$

When ammonia is added to the gold–copper–cyanide system, copper can now exist as either copper (I) or copper (II), since ammonia ligates to copper (II) and helps stabilize this oxidation state. The copper behaves similarly to the gold, with the leaching rate decreasing sharply at concentrations above 2 mM copper (I) and ammonia.

The only way in which gold can be leached at a rate above the oxygen-diffusion-controlled limit, which under these conditions corresponds to a rate of $6.2 \times 10^{-5}\,\mathrm{mol/m^2\,s}$ (Levich, 1962), is by the action of another oxidant. The most likely candidate for this other oxidant is $Cu(CN)_2^-$, which has been shown to cement onto the gold surface according to Eq. (18). This could account for the increased rate by itself, but it is also possible that, if the copper deposit is in good contact with the gold surface, it will act as a site for oxygen reduction, which, on copper, is a four-electron process (*cf.* Eq. (16)).

Drok and Ritchie's work has shown that the behaviour of the 1:1 copper (I): ammonia system is markedly different from the 1:4 system. The fact that the reaction ceases at lower copper (I) concentrations in the 1:1 case than in the 1:4 case appears to be related to a difference in the solubility of copper (I) in the two systems. They noted that a purple precipitate is formed when the copper (I) concentration exceeds about 5 mM in the 1:1 case. This purple precipitate has been reported as being due to a mixed copper–cyanide–ammonia complex (Cooper and Plane, 1966; Puvlenko and Sergeeva, 1969; Sergeeva and Puvlenko, 1967a, b; Sharpe, 1976; Williams *et al.* 1971). However in the ammonia-free system and 1:4 system, a brown precipitate of CuO is formed once the solubility limit of about 12 mM (*i.e.*, ~750 mg/L) copper (I) is exceeded.

3.1.1. Plant experience using ammonia

The experiences of plants adopting ammoniacal cyanidation would indicate that early successes were probably more fortuitous than planned and metallurgists quickly realized that there were a number of complex interactions occurring during ammoniacal cyanidation. An example of this has been elaborated in Table 2, where the addition of 250 g/t of lead nitrate had a significant impact on gold extraction. The ore in question contained chalcocite and it could perhaps have been predicted that lead might be of benefit even in the ammoniacal cyanidation test work. However, the experiences encountered at the Akjoujt Treatment of Refractory Copper Ores (TORCO) Tailing Project in Mauretania (Butcher, 1995) were not so obvious and were unexpected. Indeed, it was proposed that the mechanism for dissolution for the gold was by redox reaction in which no oxygen was needed (Costello, 1991):

$$Cu(NH_3)_2(CN)_2 + Au \rightarrow [Cu(NH_3)_2]^+ + [Au(CN)_2]^- \qquad (19)$$

The Akjoujt Project was established to recover gold from the tailing from the Guelb Mogrein copper deposit near Akjoujt, Mauretania. The TORCO process involved the heating of refractory copper-oxide minerals with salt (NaCl) and coal and recovering the resultant copper particles by flotation. Some of the gold contained in the ore is recovered in the flotation stage, but the majority remains in the tailing, which may be regarded as a synthetic magnetite. The tailing averaged 3.2 g/t gold and 0.75% copper. The plant was designed to use the Hunt Process, which involved the cyanidation of copper-bearing gold ores in the presence of ammonia. Initially the plant operated satisfactorily apart from insufficient agitator power to keep the heavy mineral in suspension, but after several months, as the tailing reclamation progressed beyond the outer zones and higher-grade material was encountered, significant recovery problems arose. The recovery was as low as 25% on some days.

The recovery problems were resolved by implementing oxygen gas injection in various stages of the cyanidation circuit. The need for oxygen addition was an unexpected event as there were no apparent oxygen consumers in the ore and laboratory testing did not predict any problems. According to Butcher (1995), the process development was undertaken on the assumption that the reaction mechanism involved in the ammoniacal cyanidation process was anaerobic. One explanation could be that the metallurgical test samples were taken from the oxidized perimeter of the dump.

The addition of oxygen had a significant effect, as shown in Table 5.

Gold extraction increased and copper solution levels were reduced markedly. Copper levels as high as 1,500 mg/L in the fifth leach tank were common prior to oxygen injection and as the trial progressed, copper levels dropped uniformly. In addition, cyanide and ammonia levels were reduced without adversely affecting gold extraction, which in turn led to a further decrease in solution copper level. Importantly, the copper profile reversed and a negative copper profile was established, falling from 200–400 mg/L in Tank 1 to 50–150 mg/L in Tank 5. The effect was quickly reversed on occasions when the oxygen sparger into Tank 1 blocked, but was equally rapidly restored when oxygen flow was re-established. These unplanned ‘tests’ indicated that the improved gold extraction was not due to feed material changes, but was caused by the higher dissolved oxygen (DO) concentration.

The plant operators concluded from their observations that the solubility of gold in the system was heavily reliant on the presence of oxygen and that the gold species can change its state quickly, going in and out of solution on a

Table 5
Effect of oxygen in the ammoniacal cyanidation of TORCO tailing (after Butcher, 1995)

Period	Average reagent consumption (kg/t)			Gold recovery (%)
	NaCN	Ammonia	Oxygen	
December 1992–August 1993	1.69	2.7	0	75.9
January 1994–December 1994	0.98	1.49	1.16	87.6

macro scale within hours. No explanation for the changed chemistry was forthcoming and the paper did not purport to present any clear understanding of the solution chemistry involved in ammoniacal cyanidation, but the conclusion can be drawn that it is a complex subject. The work undertaken by Drok and Ritchie (1997) may provide an explanation for the improved results at Guelb Mogrein.

A somewhat similar experience occurred at the Mt Gibson gold plant, which was designed to process laterite ore, which overlaid deeper mixed oxide–sulfide ore. The ore contained about 500 g/t cyanide-soluble copper, some of which was associated with sulfide mineralization and which occurred within highly weathered clay minerals.

Metallurgical laboratory testing indicated that the ore was amenable to straight cyanidation with a moderate penalty in cyanide consumption, but with high gold recovery. However, as the proportion of these ore types increased, there was a significant drop in gold recovery. Recovery dropped from >90% to as low as 55% on some days and averaged just 75% during the quarter that the author became involved in the operation. The poor metallurgical performance was exacerbated by the highly viscous nature of the ore, which rendered the leaching tanks virtually motionless; free water was noticeable on top of Leach Tank 1!

A range of remedial actions was implemented, including restoration of draft-tube agitation, introduction of liquid oxygen, as well as addition of lead nitrate and viscosity modifier. The latter attempt was almost abandoned as it was impossible to achieve any reduction in viscosity no matter what combination of alkali and viscosity modifier was tested. The breakthrough came when the viscosity modifier was added to the mill and lime was added at the leach feed pump hopper instead of the mill feed. The effect was dramatic. The cumulative effect of reagents and plant modifications resulted in recovery rising to 92%, at which point the focus switched to reducing cyanide consumption. This led to the development of the Sceresini copper/cyanide recovery process.

Shortly after the copper recovery plant was commissioned, the primary crusher failed and the plant was fed from a large stockpile of crushed laterite ore, which contained negligible copper. As expected, the copper in the circuit reduced to a low level, but when sulfide copper–gold ore processing resumed, the copper concentration in the leach circuit did not attain previous levels even though a higher copper orebody was being mined. The copper recovery plant was operated intermittently for a few months and was eventually shut down.

The combined effects of the lead and the oxygen coupled with a small amount of ammonia that was generated in the spent electrolyte during electrowinning (EW) (three strips per day) and probably ammonium nitrate (ANFO) spillage, was sufficient to hold the copper at manageable levels.

This method of operation continued for approximately 2 years when a stepwise change in the DO concentration occurred, with the introduction of a high-efficiency gas injector. The DO level increased from around 14 ppm to greater than 30 ppm and there was an immediate increase in gold recovery of about 2% and a significant 30% (about 0.5 kg/t) reduction in cyanide consumption. Surprisingly, the carbon copper loading decreased from around 3,000 to just under 2,000 g/t, while gold loading increased from 1,300 to 2,400 g/t and silver loading also increased by approximately 50%.

It was apparent that copper was being removed from the system, and the assumption was that this was by oxidation to copper (II) due to increased oxygen concentration. If cupric copper were being formed, why did cyanide consumption not increase owing to cyanate formation as per Eqs. (1)–(3)? Once again Drok and Ritchie's work (1997) provides the answer, *i.e.*, the precipitation of cyanide-insoluble cupric copper at elevated dissolved oxygen concentrations.

The implementation of a number of changes in the Mt Gibson circuit had masked the effect of oxygen to a certain degree and it was not until the boost in DO levels from about 14 to >30 ppm that the stepwise effect of the elevated oxygen concentration was noticed.

4. COPPER AND CYANIDE RECOVERY PROCESSES

Processes for the recovery of both cyanide and copper are discussed in detail in Chapter 29; these are also listed below for completeness. The processes that focus on copper recovery are dealt with in more detail below. These processes fall into two basic groups: (i) sulfide precipitation for copper recovery, and (ii) ion-exchange (resin or liquid extractant) technologies.

4.1. Sulfide-precipitation processes

"The idea of using acid or acid and a soluble sulfide for the precipitation of copper from a cyanide solution is not new". These words were by Leaver and Wolf (1931), who set out to explain what happens during cyanidation of ores for the recovery of precious metals containing various forms of copper and zinc. Anderson (1903) in an early patent specified a process for recovering precious metals from a cyanide solution by adding a soluble sulfide to the solution followed by sulfuric acid. Wheelock (1910) patented a process for the regeneration of cyanide, which included the use of acid to separate the metals and the adsorption of hydrocyanic acid into an alkaline solution. A number of processes have been developed for treating gold–copper ores and they incorporate aspects of work accomplished by these pioneering researchers. Some of these processes are still in the developmental stage, while others are yet to be adopted by the mining industry.

4.1.1. MNR process

This process, which was developed by MNR (Potter *et al.*, 1986), involves a solid/liquid separation step to obtain a clarified copper–cyanide solution, to which water-soluble sulfide compounds (NaSH or Na_2S) are added and the solution is then acidified to pH <5 by the addition of sulfuric acid to precipitate the copper. The cuprous sulfide precipitate is recovered by filtration and the hydrogen cyanide is volatilized and reabsorbed in an alkali. All reactions are conducted under a pressure of 1.5–15 bar. Other base metals present will precipitate with the copper thereby contaminating the resultant product. The potential for co-precipitation of CuCN and CuSCN are also potential issues for consideration. The residual solution must be rendered alkaline prior to discharge.

Any additional sulfide added to ensure total copper precipitation will destroy free cyanide to form thiocyanate complexes. Furthermore, the entry of oxygen into the reactors will lead to oxidation of NaSH to finely divided elemental sulfur and ultimately thiocyanates. The synthetic chalcocite (Cu_2S) recovered has an economic value; however, the copper sulfide precipitate, even with recycle, tends to be finely divided and not easily filterable. The acidification step also can lead to gypsum and calcite formation. Both of these minerals will usually lead to significant scale formation throughout the plant. There are no known commercial applications at this stage.

4.1.2. Sulfidization–acidification–recycling–thickening process

This process is a variation of the MNR process. Lower pH values are employed in order to achieve lower levels of cyanide (as CuCN) in the precipitate by disproportionation of CuCN to form Cu^o and Cu^{2+}, thereby releasing additional cyanide for recovery.

A SART plant was successfully commissioned at the Telfer Gold Mine in Western Australia during mid-2000 (MacPhail *et al.*, 1998), but only operated for a short time before Telfer entered a care-and-maintenance stage pending the outcome of an extensive drilling campaign. This exploration has resulted in the delineation of a very large resource, which is to be mined and processed at about 17 Mtpa. The SART process has been incorporated in the new plant.

4.1.3. Cutech process

The Cutech Process consisted of four principal stages:

- *Cyanidation and solid/liquid separation.*
- *Precipitation.* Following clarification, reagents are added to form a precipitate containing the gold, copper and cyanide. The remaining solution, which is cyanide free, can be discarded or reused in the process.

- *Digestion*. The precipitated solids are digested at elevated temperature; the copper is dissolved, reagents used in the precipitation stage are regenerated, hydrogen–cyanide gas is liberated and metallic-gold slime is produced.
- *Treatment of digester products*. The gold slime is suitable for direct smelting. The conventional carbon absorption, elution and electrowinning stages are completely eliminated.

The cyanide gas is absorbed in an alkaline scrubber to produce cyanide solution for leaching fresh ore and copper is recovered from the digester liquor by EW or precipitation and regenerated reagents are recycled to the precipitation stage.

The principles of the Cutech process were developed and tested in a 60 L/h pilot plant utilizing synthetic solution (Clarke, 1991), but it is unknown whether the process was tested beyond that stage. No operating cost estimates were provided, but it would appear that the process might have some potential for small-scale, high-grade mining applications. It would also be restricted to ore types that could readily be thickened and filtered to ensure high gold, copper and cyanide recovery. This would limit its application. Also, as has been found in applications of the MNR process, the wide range of ionic species that are produced in the cyanidation process and which are precipitated during the sulfide-precipitation stage, can result in extremely finely divided slimes that are almost impossible to filter. There are no known commercial applications at this stage.

4.1.4. *Sceresini process*

The Sceresini process (Sceresini and Richardson, 1991) selectively adsorbs copper onto carbon by maintaining predominantly $\mathrm{Cu(CN)}_2^-/\mathrm{Cu(CN)}_3^{2-}$ complexes by means of pH control and low free-cyanide levels prior to gold CIL . Copper/gold carbon-loading ratios of 70:1 and eluate Cu/Au ratios of about 6,000:1 are obtained from slurries assaying about 400 mg/L copper and a ~5 mg/L gold in solution. The carbon is continually eluted in a rubber-lined column using cold cyanide solution, before being returned to the last tank in the copper-CIL circuit.

The resultant cuprocyanide eluate is relatively free of contaminants that may cause the slimy precipitates obtained by direct treatment of process solutions such as in the MNR, SART and Cutech processes. Two commercial plants were built, one (Mt Gibson) precipitating CuCN at pH values of 2–2.5 and the other (Red Dome) precipitating $\mathrm{Cu_2S}$ at similar pH range, but with the addition of sodium sulfide. Both circuits utilized solids recycle to nucleate the precipitation process. Very fine-sized precipitates were formed, but each product settled rapidly and filtered rapidly to form porous filter cake.

Copper is precipitated as cuprocyanide by acidifying to pH <3. The cyanide liberated as hydrocyanic acid is converted into sodium or calcium cyanide after solid/liquid separation by raising the pH value to >10.5 with caustic soda or lime. Spent gold EW electrolyte can be used for this duty. The cuprocyanide precipitate is digested in sulfuric acid at about 80°C, using oxygen gas as the oxidant to produce copper sulfate. The HCN gas evolved is adsorbed in an alkaline scrubber.

The theoretical reagent consumption for the copper sulfate route expressed as kg/kg of copper recovered is: sulfuric acid, 4.19; oxygen, 0.15; caustic soda, 2.64 and quicklime (equivalent at 78% CaO), 2.37.

In the sulfide variation, copper can be recovered as cuprous sulfide by acidifying to a pH value of <3 and adding sodium sulfide. The sulfide precipitate is filtered and washed to remove any residual free cyanide and is a saleable product. The cyanide liberated as hydrocyanic acid is converted into sodium or calcium cyanide as above.

The theoretical reagent consumption for the copper sulfide route expressed as kg/kg of copper recovered is: sulfuric acid, 3.1; sodium sulfide, 0.613; caustic soda, 2.64 and quicklime (equivalent at 78% CaO), 2.37.

The Mt Gibson circuit is shown in Fig. 5.

The copper sulfate route was selected at Mt Gibson and the copper sulfide route at Nuigini Mining's Red Dome mine. Experience would favour the

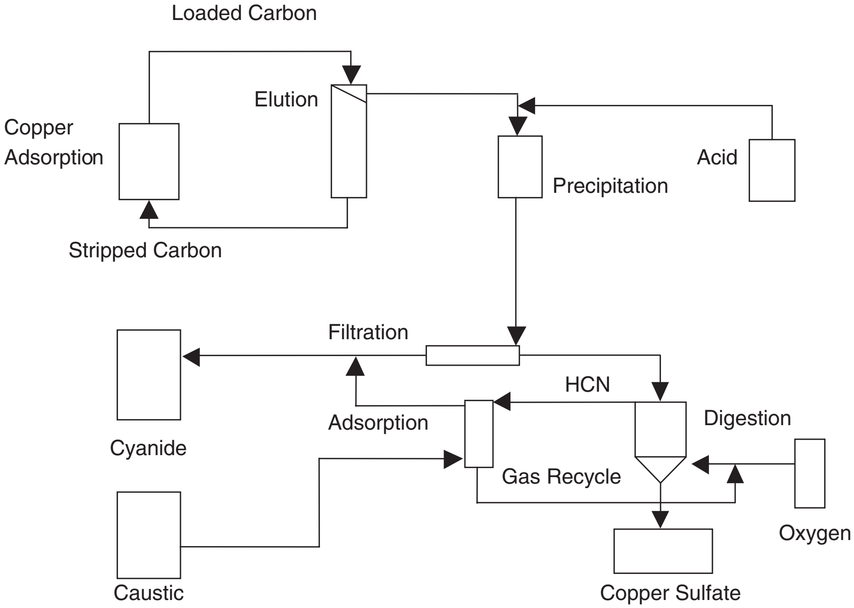

Fig. 5. Sceresini copper–cyanide recovery process schematic.

copper-sulfide route although this has the disadvantage of introducing sulfide ion to the system with the attendant problems discussed above. Future installations would consider the EW option with partial acidification/HCN volatilization of a bleed stream for CN/Cu mole ratio control below 4:1.

The Sceresini process has the advantage of pre-concentrating the copper via carbon adsorption.

4.1.5. CyanoMet R process

A modification to the MNR/SART process, the CyanoMet R process, has been proposed (Virnig and Weerts, 1993; Davis *et al*., 1998). In the detoxification of heap-leach operations, they suggested passing the aqueous effluent from the gold heap-leach pad to a conventional mixer/settler operation using an alkyl guanidine-based extractant (Cyanomet RG) using kerosene as the diluent. The metal–cyanide species were then stripped from the organic phase using a strong caustic solution and pumped to an EW cell where cyanide was destroyed by oxidation at the anode and the metals deposited as a sludge.

Davis *et al*. (1998) proposed a SX route based on LIX XI-78 to concentrate the copper to 30–40 g/L (in 50 g/L total cyanide, 10 g/L NaOH) from dilute liquors containing <1 g/L of copper and 1.7 g/L total cyanide. The more concentrated copper–cyanide solution would then be subjected to copper and cyanide separation by application of the MNR, acidification–volatalization –regeneration (AVR) or Du Pont electrolysis processes. LIX XI-78 is based upon a mixture of a quaternary amine with 4-nonylphenol (Jay, 2000). There are no known commercial applications at this stage.

4.1.6. Cyanisorb^{TM} process

The Cyanisorb$^{\mathrm{TM}}$ process is based on the direct AVR process, but differs in that the process employs high-efficiency packed towers to strip cyanide from either slurries or clear solutions at near-neutral pH, whereas the AVR process operates at pH values below 2, thereby requiring more acid. However, when copper and zinc cyanides are present, to achieve $>90\%$ WAD cyanide recovery, the solution pH must be reduced to below pH 6 and preferably, 4.5–5.5 (Stevenson *et al*., 1994).

Cyanisorb$^{\mathrm{TM}}$ recovers both free cyanide and metal–cyanide complexes. However, with respect to its application in the treatment of gold–copper ores, Cyanisorb$^{\mathrm{TM}}$, like AVR will only recover the copper-complexed cyanide but not the CuCN-bound cyanide. Cuprocyanide is precipitated and lost with the tailing residue during the treatment of tailing slurry or is precipitated with other stable cyanide complexes in the case of solution treatment. The recovery of the copper–cyanide precipitate is problematic due to the large volume of solution to be treated and frequently the poor solid–liquid separation characteristics of the mixed precipitates.

The major cost associated with these plants is the cost of both acid and the energy required to pass sufficient air through the stripping tower to volatilize all of the HCN formed. The acid cost problem is further aggravated by the reaction between sulfuric acid and any acid-soluble minerals that are present in some ores, for example, dolomite [$CaMg(CO_3)_2$].

The Golden Cross mine in Waihi, New Zealand and the NERCO DeLamar mine in southwest Idaho used the Cyanisorb^{TM} process in the 1990s.

4.2. Ion-exchange technologies – Resins

Although significant development of ion-exchange resins has taken place over the past 20 years or so, they have seen niche applications in the gold mining industry only over the past few years (Lanham, 2003) (see Chapter 25). Processes using ion-exchange resins for the recovery of cyanide have been proposed and are discussed in detail in Chapter 29. A summary of some potentially useful processes pertaining to the recovery of copper and/or cyanide is given below.

4.2.1. Oretek CPC process

A recently reported resin-based technology for copper and cyanide recovery is the Oretek CPC process (Jay, 2000, 2003a, b). The company has been developing a range of solvated super-hydrophilic ion-exchange and -capturing polymers for copper and other metal ions, with displacement of cyanide. The metal ion can then be directly recovered under alkaline conditions from the polychelator by EW, cementation, precipitation or other suitable method. Cathode copper can be recovered in a conventional EW membrane cell and the cyanide returned to the leach circuit.

No changes are made to the process solution chemistry, no hydrogen cyanide gas is generated and no lime or other chemicals are needed to change the alkalinity or acidity of the tailing slurry. The direct adsorption of copper cyanide from the leach circuit prior to the carbon-adsorption circuit would be beneficial when the process water is highly saline as this prevents excessive copper loading on the carbon with attendant higher carbon inventory and copper reporting to the gold bullion. There are no known commercial applications at this stage.

4.2.2. Vitrokele^{TM}

Research conducted at McGill University, Montreal, Canada in the early 1980s led to the development of a technology for the recovery of cyanide and cyanide metal complexes. (Holbein *et al.*, 1988; Elvish and Huber, 1988; Whittle, 1992). The ligands bound to the polystyrene resin structure were not identified but V912 is believed to be of a Type I quaternary amine functionality.

An economic study into the pilot-scale application of Vitrokele 912 at the Gabanintha mine, Meekathara, Western Australia has been reported (Holbein *et al.*, 1989; Johnson, 1991), with >99% recovery of cyanide and copper. The project did not go ahead as the payback period for a full-scale plant exceeded the remaining life of the mine.

A commercial heap-leach plant at Connemara in Zimbabwe using the Vitrokele ion-exchange resin for gold, copper and free-cyanide recovery is said to have operated satisfactorily for a number of years (Jay, 2000).

4.2.3. Elutech process

The Elutech technology is based on the use of commercial resin to recover gold, copper and other base metals from plant liquors during the cyanidation of gold ores. A full-scale demonstration plant was constructed at the May Day mine in New South Wales and it effectively processed a cyanidation liquor containing gold, silver, copper and zinc, with cyanide levels in the barren liquor of less than 50 mg/L (Tran *et al.*, 2000). Strong-base ion-exchange resins are used to load all of the metal–cyanide complexes. A strong base, Type I ion-exchange resin, Purolite® A500, was employed in the demonstration facility, but the authors noted that Vitrokele® 912, Amberlite® IRA900 and Dowex® MSA1 performed in a similar manner.

Copper is eluted from the resin using an oxidative-acid strip solution to form copper sulfate for conventional metal recovery by either SX/EW or precipitation as copper hydroxide. The hydrocyanic acid that is generated is passed to a packed column where HCN gas is volatilized using air and then absorbed in 0.1 M sodium hydroxide and recycled. After several loading and stripping cycles the resin is then subjected to a hot (60°C) zinc *tetra*cyanide solution to elute the gold and silver cyanides, which are then recovered in a conventional EW cell. The resin loaded with zinc cyanide was then regenerated using sulfuric acid.

It is also claimed that ongoing research indicated that the technology may also be able to remove thiocyanate for cyanide recycling, but no details were provided as to how this might be achieved. There are no known commercial applications at this stage.

4.2.4. Augment process

The augment process (Le Vier *et al.*, 1997) relies on the selective adsorption of gold and silver over copper and addresses the recovery of the copper cyanides from the CIP tailing. The copper-containing ore is leached with a cyanide solution in which the molar ratio of CN/Cu is >3:1, then the metal–cyanide solution is contacted with a commercially available strong-base anion-exchange resin to adsorb gold and copper cyanides. The loaded ion-exchange resin is recovered and treated with an eluant containing copper cyanide at a CN/Cu ratio of 3.5–4:1 and a copper concentration of $>10\,g/L$ to partially elute the gold and the copper cyanide and produce an eluate with a CN/Cu ratio of $<4:1$. Spent electrolyte from the copper EW section can be used as the eluant. It is important that during the copper EW stage, the CN:Cu molar ratio remains below 4:1 to prevent cyanide oxidation to cyanate at the anode.

The copper metal along with any gold metal is electrowon from the eluate. The copper EW cells are conventional, similar to acid-based EW copper cells in design with two exceptions: (1) the solution pH value is 10.5–11 in a cyanide media; and (2) membrane technology is used to prevent oxidation of cyanide to cyanate. Copper cathode is produced at grades 99.8% copper and higher. London Metal Exchange (LME) grade prices can be realized if the metal product is further refined to 99.99% copper.

The eluted resin is treated with sulfuric acid to precipitate CuCN throughout the resin. This CuCN will then aid in the further loading of cyanide ions onto the resin. The treatment prepares the resin to be returned to the resin loading section and removes cyanide on the resin as HCN in a liquid form. HCN regeneration is conducted in a closed vessel that is vented to a lime or caustic soda scrubber. The stable HCN liquid is treated in a lime scrubber to produce calcium cyanide, $Ca(CN)_2$, which is recycled to the leach circuit. There are no known commercial applications at this stage.

4.2.5. Hannah process

The Hannah process also uses a strong-base resin to extract anionic cyanide complexes and free cyanide (Thorpe and Fleming, 2003). It can be optimized to either extract or reject thiocyanate to the final tailing, but it does not extract cyanate. Extraction efficiencies are very high, producing $<1\,mg/L$ cyanide, copper and zinc in the final tailing in only two or three extraction stages. The process is especially well suited to the extraction of copper cyanide, but is also able to extract free cyanide very efficiently, as well as other metal–cyanide complexes. The process can be applied to either solutions or pulps and operates at the normal pH range of gold plant tailings, namely pH 9–11.

The resin is eluted under ambient conditions with about 2 bed volumes of eluant in 1–2 h and is regenerated before recycling to adsorption. The eluate is treated to precipitate metals and release free cyanide, which is then recycled to leach as a concentrated cyanide solution, without having to go through an AVR-type process, a potentially attractive feature for operators. There are no known commercial applications at this stage.

4.3. Ion-exchange technologies – solvents

The process developed by the UBC (Dreisinger *et al.*, 1995), relies on selective copper solvent-extraction using XI 7950, a guanidine-based solvent extractant produced by Cognis, which has been found effective at recovering copper-cyanide species from leach liquors. The copper-loaded XI 7950 can be stripped at pH values above 12 into a concentrated copper-cyanide solution that is amenable to copper recovery using a membrane (Nafion 417) electrolysis cell. The authors claim that cyanide is not oxidized and may be recovered from a bleed solution to be returned to the leach circuit; the prevention of cyanide oxidation requires a great deal of care and further work is required in this area.

The process has four primary steps: (1) SX recovery of copper-cyanide complexes from leach solutions using XI 7950; (2) stripping of copper from the loaded organic using a high pH, copper/cyanide-rich spent electrolyte; (3) membrane-cell electrolysis of the strip solution to produce metallic copper and free cyanide for subsequent recovery and (4) cyanide recovery from a bleed stream from electrolysis.

The guanidine-based solvent extractant XI 7950 is similar to the LIX 79 reagent that was developed to extract gold-cyanide species, but is formulated to provide higher copper loading capacities than LIX 79. The extractant is a modest-strength anion exchanger.

Metal extraction and stripping proceed by the following reactions:

Loading

$$\mathrm{Na_2Cu(CN)_3 + 2R + 2H_2O \rightarrow Cu(CN)_3(RH)_2 + 2NaOH} \tag{20}$$

Stripping

$$\mathrm{Cu(CN)_3(RH)_2 + 2NaOH \rightarrow Na_2Cu(CN)_3 + 2R + 2H_2O} \tag{21}$$

Electrowinning

In a non-membrane electrolysis cell, cyanide is oxidized at the anode according to the equation

$$\mathrm{NaCN + 2NaOH \rightarrow NaCNO + H_2O + 2Na^+ + 2e} \tag{22}$$

With the membrane in place, the electrochemical reactions become

Anode

$$\mathrm{4NaOH \rightarrow O_{2(g)} + 2H_2O + 4Na^+ + 4e} \tag{23}$$

Membrane

$$\mathrm{4Na^+{}_{(anolyte)} \rightarrow 4Na^+{}_{(catholyte)}} \tag{24}$$

Cathode

$$4Na^+ + 4Na_2(CuCN)_3 + 4e \rightarrow 4Cu + 12NaCN_{(aq)} \tag{25}$$

Overall

$$4NaOH + 4Na_2Cu(CN)_3 \rightarrow O_{2(g)} + 2H_2O + 4Cu + 12NaCN_{(aq)} \tag{26}$$

There is a side reaction that takes place in copper EW from cyanide that has to be carefully controlled. Significant amounts of hydrogen gas can be evolved at the cathode under conditions of high current density or high CN_T/Cu ratios (>4) in solution. The chemistry for the side reaction is:

Cathode

$$4H_2O + 4Na^+ + 4e \rightarrow 2H_{2(g)} + 4NaOH \tag{27}$$

Overall

$$4NaOH_{(anolyte)} + 2H_2O \rightarrow O_{2(g)} + 2H_{2(g)} + 4NaOH_{(catholyte)} \tag{28}$$

The net effect of the side reaction is to waste current by decomposing water to oxygen and hydrogen and transferring sodium hydroxide to the catholyte.

Dreisinger *et al.* (1995) have suggested two options to control cyanide oxidation during electrolysis of copper cyanide solution. The first option (Fig. 6(a)) was to take a bleed stream from the primary EW circuit and to electrolyse the copper in the stream to a low level to produce a cyanide-rich solution, the potential drawback being the loss of current efficiency with increasing CN/Cu ratio in solution and the hydrogen evolution reaction shown above becomes more prevalent.

The second option suggested for cyanide recovery (Fig. 6(b)) was to acidify a bleed stream using the AVR process to precipitate CuCN and generate HCN gas, which can be adsorbed in alkaline solution. The solid CuCN is recycled to the EW circuit to maintain optimal CN_T:Cu molar ratio. This would maximize copper removal from the circuit, the only drawback being the consumption of sulfuric acid (stoichiometry: 1 kg/kg NaCN), because CuCN precipitation occurs at pH values below 3. The acid consumption may be minimized by partial acidification to pH ~7 and using compressed air injection into a circulating bleed stream of the electrolyte to volatilize cyanide as HCN, which is then adsorbed into caustic soda. The actual acid consumption is a function of the solution chemistry, but the Mt Gibson copper eluate required approximately 7 kg/m^3 to drop the eluate pH to 7 and about 21 kg/m^3 to reduce the pH to ~2.5, which was the required pH to precipitate all of the copper as CuCN.

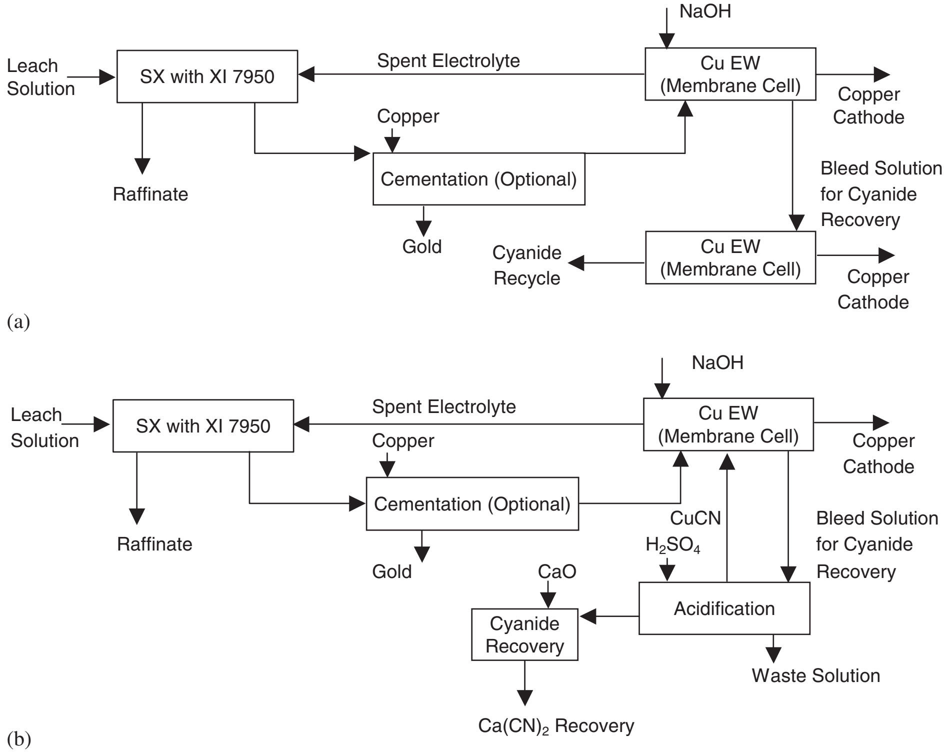

Fig. 6. (a) Flow diagram for the SX–EW recovery of copper and cyanide with a copper EW circuit for metal recovery and cyanide recycle (after Dreisinger *et al.*, 1995). (b) Flow diagram for the SX–EW recovery of copper and cyanide with a AVR process for cyanide recycle (after Dreisinger *et al.*, 1995).

The AVR chemistry is:

Acidification

$$2NaCN + H_2SO_4 \rightarrow 2HCN_{(g)} + Na_2SO_4 \qquad (29)$$

$$Na_2Cu(CN)_3 + H_2SO_4 \rightarrow CuCN_{(s)} + 2HCN + Na_2SO_4 \qquad (30)$$

Cyanide Recovery

$$CaO + 2HCN \rightarrow Ca(CN)_{2(aq)} + H_2O \qquad (31)$$

4.4. Electrowinning

Recent research conducted at the UBC (Lu *et al.*, 1999) studied the mechanisms of the anodic oxidation of copper cyanide on graphite anodes in alkaline solution. Copper was found to have a significant catalytic effect on cyanide oxidation, with cuprous cyanide oxidizing to cupric cyanide complexes under certain conditions, further reacting to form cyanate. The CN:Cu ratio was found to be critical in determining cell efficiency.

A second study by the same researchers (Lu *et al.*, 2002) examined the anodic behaviour of alkaline solutions containing copper cyanide and sulfite on the graphite anode. The work showed that sulfite may be added to copper cyanide solutions to reduce cyanide oxidation at the anode during copper EW. Anodic sulfite oxidation is enhanced in the presence of copper cyanide. Sulfite also suppresses the oxidation of copper cyanide. The effect of sulfite on the oxidation of copper cyanide decreases with increasing mole ratio of cyanide to copper. This is related to the shift in the discharged species from $Cu(CN)_3^{2-}$ to $Cu(CN)_4^{3-}$ with increasing mole ratio of cyanide to copper. Sulfite is oxidized to sulfate.

As well as further development of high-efficiency membrane cells, recent developments in EW cell designs may also have application to reduce cyanide oxidation in cuprocyanide electrolysis. Examples of cells that provide high mass-transfer efficiency by employing high solution flowrates to minimize boundary layer effects and diffusion rate control include the Electrometals EMEW® Cell (Treasure, 2000), and more recently the Jetcell® (Jayasekera, 2003).

5. ALTERNATIVE LIXIVIANTS

5.1. Thiosulfate leaching

Environmental and public concerns over the use of cyanide in the recovery of gold, has led to a drive towards developing alternative leaching technologies. Among the more promising leach systems, copper promoted, ammoniacal thiosulfate leaching technology is emerging as an alternative to cyanidation for gold extraction (Jiang *et al.*, 1993; Muir and Alymore, 2004). This is discussed in detail in Chapter 22; however, the implications of application to high-copper gold ores warrant some consideration here.

Copper is usually added as an oxidant to promote gold leaching in ammoniacal thiosulfate solution and it has been found that the addition of copper powder will precipitate gold from thiosulfate solution (Guerra and Dreisinger, 1999; Choo and Jeffrey, 2004). Electrochemical studies of the cathodic reaction, gold deposition, were carried out. It was found that a high overpotential is required to deposit gold onto a gold substrate. However, the presence of copper, either as metallic copper or as Cu(I) thiosulfate, dramatically enhances the gold deposition half reaction. Without this enhancement, the cementation reaction would occur at a very low rate.

Resin-in-pulp for the recovery of gold and copper from ammonium thiosulfate leach liquors has been investigated, with encouraging results (Zhang and Dreisinger, 2002). The presence of copper was found to greatly lower the stability of the ammonium thiosulfate solution due to copper-catalysed thiosulfate oxidation and formation of copper sulfides or hydroxides, depending on the conditions. *Tetra*thionate, as the product of thiosulfate oxidation, strongly poisoned the resins. Good selectivity for gold over copper was obtained. The metals were eluted with a mixed solution of Na_2SO_3 and NH_3. Molleman and Dreisinger (2002) studied the behaviour of thiosulfate, tetrathionate and sulfate in leach solutions using ion chromatography. Their experiments showed that both gold extraction and thiosulfate stability were affected by a combination of aeration and cupric ions in solution and that it was important to establish a balance between providing sufficient air and cupric ions for fast gold dissolution and at the same time minimize the amount of air in the presence of cupric ions to prevent excessive thiosulfate degradation.

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Bruno Sceresini has 40 years of diversified metallurgical experience in Australia including milling, concentration, nonferrous pyrometallurgy involving smelting and refining, hydrometallurgy involving electrowinning, pressure leaching, hydrogen gas reduction and gold cyanidation including refractory-ore treatment, Merrill–Crowe precipitation, CIP and heap leach. He developed and patented the Sceresini process for cyanide and copper recovery from copper/gold ores. He qualified with an MAusIMM and Associateship in Metallurgy, West Australian School of Mines.

Bruno was closely involved in the development and application of enhanced mass transfer and reaction technology, especially in the field of gas dispersion and reaction in slurries and spent almost 10 years with worldwide marketing responsibility for the technology in aeration/leaching applications and for contaminated effluent treatment.

He also played a key role in the implementation of a significant R&D programme, which funded the design and construction of a 25 t/h modular mineral-processing plant utilizing state-of-the-art technology.

Bruno is presently involved in metallurgical consulting and in developing enhanced oxidation technologies including generation and application of ozone gas for mineral processing and waste-stream treatment, in particular gold-plant cyanidation tailing products. His managerial experience includes various Project Management and General Manager/Managing Director roles; Bruno is a director of a listed junior mining company.

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Chapter 33

Case study flowsheets: copper–gold concentrate treatment

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1. INTRODUCTION

The conventional treatment of copper–gold concentrates involves smelting, converting and electro-refining to produce a copper-cathode product. Sulfur in the copper concentrates is oxidized to sulfur dioxide during smelting and converting and is normally used to make by-product sulfuric acid. Iron in the copper concentrates reports to the slag, along with many impurity elements. Precious metals (Au, Ag and platinum-group metals (PGMs)) are recovered from the anode slimes produced by the electro-refining operation. The conventional treatment of copper concentrates by this method works well and recovers copper and precious metals as high-value products. Processes for the recovery of gold from polymetallic ores in general are discussed in Chapter 35, while the recovery of gold along with PGMs is detailed in Chapter 36.

The conventional treatment of copper–gold concentrates does elicit some compelling reasons to seek an alternative hydrometallurgical process for recovery of concentrate values. These include the following:

1. *Capital cost.* The capital cost of smelter and refinery complexes is very high. The typical range of cost is \$3,000–\$5,000 (US\$) investment per annual tonne of copper production (*e.g.*, \$900 million to \$1.5 billion for 300,000 tpa Cu production). The unit cost will vary according to scale and location. The high capital cost of smelters/refineries is partly offset by low operating costs. Nevertheless, a less capital-intensive copper production process would be advantageous.

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2. *Impurity tolerance*. Smelters are limited in their ability to treat concentrates that contain significant deleterious elements. Concentrates that contain high levels of impurities such as selenium, tellurium, mercury, arsenic, antimony, bismuth, fluoride and chloride may incur large financial penalties under currently prevailing smelter contract specifications. Alternatively, at some impurity level, it may not be possible at all for the smelter to treat the concentrate. This is obviously a significant problem for producers of "dirty" concentrates.
3. *Lower-grade copper–gold concentrates*. Gold is frequently associated with copper concentrates. In some cases, high recoveries of gold by flotation are accompanied by high levels of pyrite flotation, resulting in a low-grade copper concentrate for treatment. Smelting of low-grade concentrates incurs significant economic penalties in shipping of concentrates to smelters, unit deductions in smelter contracts and treatment and refining costs. These charges are justified, in that the smelter must now treat large amounts of barren pyrite to make slag and sulfur products. In this case, alternatives to smelter/refinery treatment of concentrates may become attractive, especially where more dilute concentrate grades benefit economics.
4. *Mine to market optimization*. One of the trends in mining and mineral processing has been to optimize the economics of the mining and milling operations in concert, the so-called *mine-to-mill* concept. Increasingly, it makes sense to carry this global thinking right through to the copper-production process and the ultimate market. It may well make sense to the overall economics of a mining operation to account for (i) production of a lower-grade concentrate with higher overall recovery of copper from the mine, (ii) treatment of the lower-grade copper concentrate at the minesite to make copper metal, and (iii) use of by-product weak acid from the copper-recovery process as a reagent to leach and recover copper at the minesite. The overall economics to be achieved using this approach may give an advantage to an alternative to smelting.
5. *Recovery of valuable by-products*. Copper concentrates may often contain significant levels of base and precious-metal by-products. Copper smelters are efficient at the recovery of gold, silver and PGMs but often pay poorly and with much delay for these elements. Base metals such as zinc, cobalt and nickel are difficult to recover through a copper-smelter process. In each of these cases, an alternative to smelting may be attractive.
6. *Use of existing capital*. In several cases, copper heap-leach-SX/EW process plants are running out of ore feed. These plants have fully functional SX/EW plants available for further copper recovery as electrowon cathode. In these cases, it may make sense to adopt a copper–gold concentrate hydrometallurgy process as the *front end* of the process plant and further utilize existing capital.

7. *Economics*. Smelter economics are more scale sensitive than hydrometallurgical alternatives. Hydrometallurgical plants are more suited to application of modular incremental project development if required.

Copper hydrometallurgy has been extensively studied as an alternative route to chalcopyrite concentrate treatment. Historically, a large number of hydrometallurgical treatment processes have been developed to treat copper concentrates (Demarthe *et al.*, 1976; Schweitzer and Livingstone, 1982; Dalton, 1991; Swinkels and Berezowsky, 1978; Vizsolyi, 1967; Kuhn *et al.*, 1974; Kruesi *et al.*, 1973; Bruynesteyn and Duncan, 1971; Peters *et al.*, 1981; Everett, 1994; Jones, 1996; Corrans *et al.*, 1995).

These processes have all failed to achieve sustained commercial production due to one or more of the following list of shortcomings:

- Low copper recovery in the primary leach step
- Copper loss due to copper co-precipitation with iron-hydrolysis products
- Difficult or incomplete gold, silver and platinum-group-metal recovery from leach residue
- Unconventional and difficult electrolysis step
- Difficult elemental-sulfur recovery step from leach residue
- Excessive corrosion (especially chloride circuits)
- Difficulty in fixing toxic by-products in a stable waste-product
- Large energy requirements for mixing and oxygen dispersion
- Poor-quality copper product that requires electrorefining.

In addition, a number of other barriers have mitigated commercial success. New technology risk and the cost of commercial licensing have effectively stopped a number of promising developments.

Against this backdrop, significant advances have been made over the last few years in advancing the use of hydrometallurgy for copper ore and concentrate treatment. At the time of writing this chapter at least four separate commercial plants have started or are under construction for copper recovery from sulfate medium:

1. *Mt. Gordon copper process* (Richmond and Dreisinger, 2002). The Mt. Gordon Copper Process started in 1998 at the Mt. Gordon Copper site in Queensland, Australia. This process recovers copper from chalcocite-pyrite ores or concentrates by low-temperature pressure leaching, copper SX–EW. The plant has operated at up to 50,000 tpa Cu production at a cash cost (US$) of as low as $0.31/lb of copper from mining through to metal production (Dreisinger *et al.*, 2002b).

2. *Phelps Dodge total pressure oxidation plant* (Marsden *et al.*, 2003). The Phelps Dodge Total Pressure Oxidation Process demonstration plant commenced in May 2003. The plant was designed to recover 16,000 tpa of Cu by autoclave leaching at 220–230°C followed by CCD washing of the autoclave residue and copper SX–EW. The key design feature of this plant is the use of acid from the autoclave oxidation of concentrates for acid makeup to an associated copper stockpile leach.
3. *Alliance copper BIOCOP^{TM} Process* (Dew and Batty, 2003). The Alliance Copper group is a joint venture between BHP Billiton and Codelco to exploit the use of bioleaching for treatment of copper concentrates. The BIOCOP^{TM} process involves the use of extreme thermophile bacteria for copper leaching. The process involves a pre-treatment step and then two stages of bioleaching. The bioleach discharge solution is recovered and sent to conventional SX–EW for copper recovery. Alliance have started a 20,000 tpa copper production plant in Chile.
4. *Oxiana Sepon copper process* (Baxter *et al.*, 2003a, b). Oxiana Resources are currently developing the Sepon Copper project in Laos, South East Asia. The Sepon ore contains predominantly chalcocite with pyrite and clayey gangue in the ore. The metallurgical flowsheet designed for the plant (and now under construction) uses atmospheric leaching followed by SX–EW recovery of copper. The barren washed tails are floated to recover a pyrite/elemental sulfur concentrate. The concentrate is oxidized at 225°C to produce a final solution containing acid and ferric sulfate. This autoclave solution is applied in the atmospheric leach.

On the chloride side, Outokumpu have commissioned a 1 tpd Cu pilot plant for the Hydrocopper process. The Hydrocopper process (Hämäläinen *et al.*, 2003) produces chlorine, caustic and hydrogen using a conventional chloro-alkali cell. These reagent products are applied to leach chalcopyrite (chlorine), raise the pH to precipitate cuprous oxide (caustic) and reduce the cuprous oxide to metal (hydrogen). This process represents a significant innovation, in that electrochemistry is used in the manufacture of chemicals, not the winning of metals. This overcomes the Hydrocopper process from difficulties associated with production of copper metal, such as dendrite formation. The challenge of separating copper dendrites from cathode blanks and removing the dendrites from the cell has been challenging for all processes (*e.g.*, CLEAR, DEXTEC, INTEC, CUPREX) that employ direct electrowinning (EW) of copper.

The methods for copper recovery from copper–gold concentrates are therefore increasingly well established. In each of the sulfate process cases above, precious metals are not present in economic quantities in the feed material. In general, the recovery of gold and other precious metals from such copper–gold concentrates has yet to achieve commercial success.

2. BACKGROUND – SULFIDE LEACHING

The leaching of sulfide minerals can proceed by a variety of routes. These include oxidative, reductive and non-oxidative chemistries. Reductive and non-oxidative chemistries, while interesting and potentially very useful, are beyond the scope of this Chapter.

With oxidative leaching, sulfide minerals can be oxidized by various oxidants including for example, molecular oxygen, ferric sulfate or ferric chloride, cupric chloride or chlorine. Both the sulfide mineral oxidation and the reduction of the various oxidants are governed by the thermodynamics of the system. One way of picturing the thermodynamics of a particular system is to draw a potential – pH diagram. Fig. 1 shows the potential – pH diagram for the Cu–Fe–S–H_2O system at 25°C.

This figure shows that chalcopyrite is stable at reduced potential. Upon oxidation under acidic conditions, chalcopyrite will alter to bornite, chalcocite,

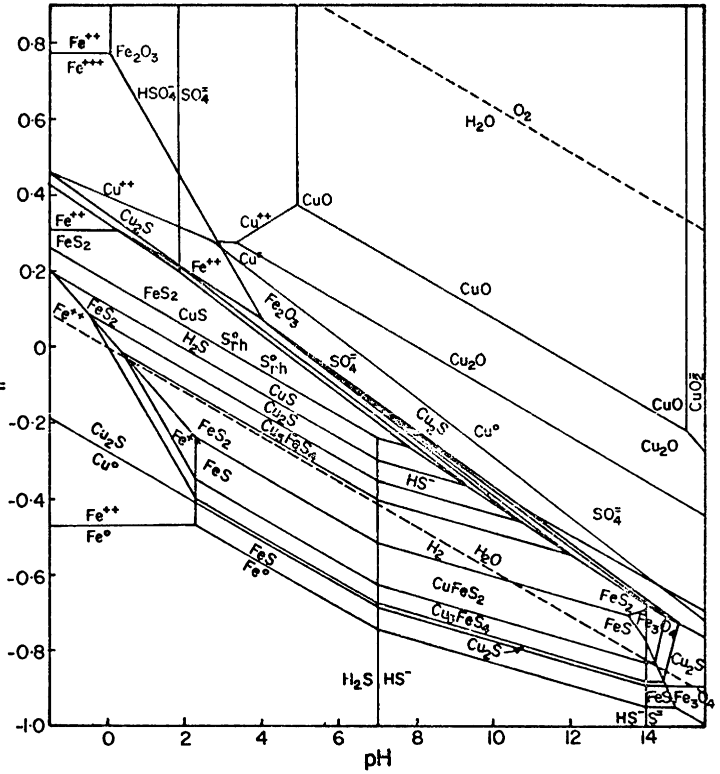

Fig. 1. The Eh–pH diagram for the Cu–Fe–S–H_2O system at 25°C; all solutes at 0.1 mol/L activity except Cu^{2+} = 0.01 mol/L (after Peters, 1973).

covellite and finally to copper ion in solution. It should therefore be possible to leach chalcopyrite under acidic oxidizing conditions.

In practice, chalcopyrite is one of the most difficult sulfide minerals to leach. Various experimental studies and reviews of chalcopyrite leach chemistry have been conducted (Wadsworth, 1972; Roman and Benner, 1973; Dutrizac and MacDonald, 1973, 1974; Habashi, 1978; Dutrizac, 1978, 1981, 1982; Jones and Peters, 1976; Munoz *et al.*, 1979; Beckstead, 1976; Majima *et al.*, 1985).

Chalcopyrite ($CuFeS_2$) chemistry can be described in the chemistry of the individual elements of Cu, Fe and S. Copper is typically leached in sulfate media to form copper sulfate in solution. Iron may be leached as either ferrous or ferric sulfate and may subsequently hydrolyze as ferric hydroxide, goethite ($FeO(OH)$), jarosite ($H_3OFe_3(SO_4)_2(OH)_6$) or hematite (Fe_2O_3). Sulfide sulfur in chalcopyrite may oxidize to elemental sulfur or through to sulfate sulfur. The overall chemistry of leaching can be dramatically impacted by the final state of the copper, iron and sulfur. Acid and oxidant consumption can be affected. This is shown in the following series of chemistries.

Chalcopyrite leaching with ferrous sulfate and elemental sulfur reaction products:

$$CuFeS_2 + O_2 + 2H_2SO_4 \rightarrow CuSO_4 + FeSO_4 + 2S + 2H_2O \tag{1}$$

Chalcopyrite leaching with ferric sulfate and elemental sulfur reaction products:

$$CuFeS_2 + 1.25O_2 + 2.5H_2SO_4 \rightarrow CuSO_4 + 0.5Fe_2(SO_4)_3 + 2S + 2.5H_2O \tag{2}$$

Chalcopyrite leaching with ferric hydroxide and elemental sulfur reaction products:

$$CuFeS_2 + 1.25O_2 + H_2SO_4 + 0.5H_2O \rightarrow CuSO_4 + Fe(OH)_3 + 2S \tag{3}$$

Chalcopyrite leaching with goethite and elemental sulfur reaction products:

$$CuFeS_2 + 1.25O_2 + H_2SO_4 \rightarrow CuSO_4 + FeO(OH) + 2S + 0.5H_2O \tag{4}$$

Chalcopyrite leaching with jarosite and elemental sulfur reaction products:

$$\begin{aligned} CuFeS_2 + 1.25O_2 + 1.67H_2SO_4 \rightarrow {} & CuSO_4 + 0.333H_3OFe_3(SO_4)_2(OH)_6 \\ & + 2S + 0.167H_2O \end{aligned} \tag{5}$$

Chalcopyrite leaching with hematite and elemental sulfur reaction products:

$$CuFeS_2 + 1.25O_2 + H_2SO_4 \rightarrow CuSO_4 + 0.5Fe_2O_3 + 2S + H_2O \tag{6}$$

Chalcopyrite leaching with ferric sulfate and sulfate reaction products:

$$CuFeS_2 + 4.25O_2 + 0.5H_2SO_4 \rightarrow CuSO_4 + 0.5Fe_2(SO_4)_3 + 0.5H_2O \tag{7}$$

Chalcopyrite leaching with ferric hydroxide and sulfate reaction products:

$$CuFeS_2 + 4.25O_2 + 2.5H_2O \rightarrow CuSO_4 + Fe(OH)_3 + H_2SO_4 \quad (8)$$

Chalcopyrite leaching with goethite and sulfate reaction products:

$$CuFeS_2 + 4.25O_2 + 1.5H_2O \rightarrow CuSO_4 + FeO(OH) + H_2SO_4 \quad (9)$$

Chalcopyrite leaching with jarosite and sulfate reaction products:

$$CuFeS_2 + 4.25O_2 + 1.83H_2O \rightarrow CuSO_4 + 0.333H_3OFe_3(SO_4)_2(OH)_6 + 0.333H_2SO_4 \quad (10)$$

Chalcopyrite leaching with hematite and sulfate reaction products:

$$CuFeS_2 + 4.25O_2 + H_2O \rightarrow CuSO_4 + 0.5Fe_2O_3 + H_2SO_4 \quad (11)$$

With elemental sulfur as a reaction product, the use of oxygen varies between 1 and 1.25 moles per mole of Cu (equivalent to 0.5–0.63 t O_2/t Cu). With sulfate as a reaction product, oxygen consumption is 4.25 mol/mol Cu (equivalent to 2.15 t O_2/t Cu). The reagent consumption for the so-called *total oxidation* of chalcopyrite is therefore large.

The sulfuric acid balance is interesting. According to the various chemistries shown, acid is consumed when elemental sulfur and/or ferric sulfate are produced. Whenever sulfur is oxidized to sulfate and iron is precipitated, acid is produced as a net reaction product of leaching. In the case of jarosite precipitation, the production of acid is reduced due to the incorporation of sulfate in the jarosite iron-precipitate structure.

The kinetics of chalcopyrite leaching are often slow in sulfate systems. At lower temperatures (<110°C), chalcopyrite leaches slowly and tends to accumulate elemental sulfur and iron-precipitate product layers. Diffusion through the product layers tends to slow leaching. It is also believed that a passive film forms on the chalcopyrite surface that suppresses the rate of reaction. This passive film is believed to be a copper *poly*sulfide (Hackl *et al.*, 1995a, b). In this case the kinetics of copper leaching can be promoted by fine grinding or by addition of small amounts of chloride. Silver-catalysed leaching has also been successful in breaking down the passive film and promoting high extractions of copper.

At medium temperatures (~150°C), initial chalcopyrite leaching kinetics are faster. However, liquid elemental sulfur tends to block the chalcopyrite surface on partially leached particles and prevents full extraction. This can be overcome with the use of surfactants and a medium fine-grind of the concentrate (Hackl *et al.*, 1995a, b; Dempsey and Dreisinger, 2003).

At higher temperatures (>180°C), chalcopyrite leaches quickly and completely with high elemental sulfur oxidation to sulfate. At 220°C, leach times of less than 1 h are sufficient for copper extractions in excess of 98% (King and Dreisinger, 1995; Marsden *et al.*, 2003).

3. COPPER–GOLD CONCENTRATE TREATMENT PROCESSES

Based on the chemistry of chalcopyrite dissolution reviewed above, it is now possible to look at different case studies for copper–gold concentrate treatment processes. Fig. 2 shows a simplified block diagram to describe these processes. Copper must generally be leached, the copper-leach solutions are purified and finally copper is recovered. Gold is leached and recovered from the copper-leach residue.

The sulfate processes for copper recovery from copper–gold concentrates that have been commercialized or are under active development are listed in Table 1. These are listed in alphabetical order for simplicity of reference.

The Activox Process (Corrans *et al.*, 1995), the CESL Process (Jones, 1996), the Dynatec Process (Kofluk and Collins, 1998) and the MIM Albion Process (Hourn and Halbe, 1999) have been known for some time and are well represented in the literature. In this chapter, the focus will be to review a number of newer sulfate processes that show particular commercial promise for advancing the state of the art in the treatment of copper–gold ores. These will include the Phelps Dodge Total Pressure Oxidation Process, the BIOCOP^{TM} Process, the Anglo American Corporation/University of British Columbia process, for chalcopyrite concentrate leaching, and the PLATSOL$^{®}$ process for co-recovery of base and precious metals from sulfide concentrates. On the chloride side, the INTEC$^{®}$ copper process (Everett, 1994) is well known and will not be discussed. The Outokumpu Hydrocopper Process (Hämäläinen, 2003) was developed more recently and will be reviewed here. Further review of process options for copper–gold concentrates can be found in Dunne *et al.* (1999).

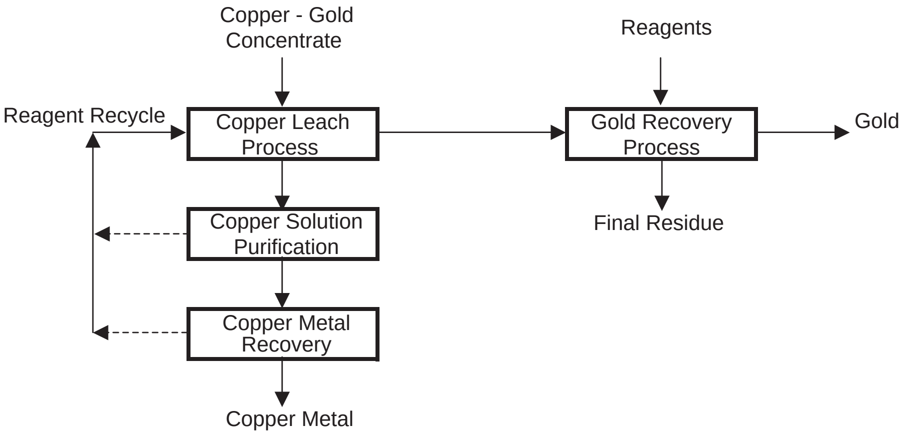

Fig. 2. Block flowsheet for hydrometallurgical treatment of copper–gold concentrates.

Table 1
Sulfate-based Copper hydrometallurgy processes for ore or concentrate treatment

Process	Status	Temperature (°C)	Pressure (atm)	Regrind D80 (μm)	Special conditions
Activox® process	D	90–110	10–12	5–10	Fine grinding combined with high oxygen overpressure overcomes chalcopyrite passivation.
Anglo American University of British Columbia Process	P	150	10–12	10–15	Modest regrind combined with surfactants for chalcopyrite leaching
Bioleach processes	P; C	35–75	1	5–10 (low-Temperature) 37 (high-Temperature)	Low-Temperature bioleach (35–50°C) requires very fine grind to overcome chalcopyrite passivation. High-Temperature bioleach (65–75°C) uses thermophilic bacteria
CESL Copper process	D	140–150	10–12	37	Chloride-catalysed leach of chalcopyrite producing basic copper sulfate precipitate in the autoclave.
Dynatec process	P	150	10–12	37	Chalcopyrite is leached using low-grade coal as an additive
MIM Albion process	P	85	1	5–10	Atmospheric ferric leaching of very finely ground concentrate
	C	90	8	100	

Table 1 (*continued*)

Process	Status	Temperature (°C)	Pressure (atm)	Regrind D80 (μm)	Special conditions
Mt. Gordon process					Pressure oxidation of chalcocite/ pyrite ore or bulk concentrate in an iron-sulfate-rich electrolyte
PLATSOL® process	P	220–230	30–40	15	Total pressure oxidation in the presence of 10–20 g/l NaCl. Precious metals leached at the same time as base metals
Oxiana Sepon	P and soon C	80: copper	Atm	100	Atmospheric ferric leach for copper from chalcocite.
		220–230: Pyrite	30–40	50	Pressure oxidation of pyrite concentrate to make acid and ferric sulfate for copper leach
Total pressure-oxidation process	C	200–230	30–40	37	Extreme conditions of Temperature and Pressure designed to rapidly destroy chalcopyrite and other sulfides

Note: Status: P Pilot Plant, D Demonstration Plant, and C Commercial Facility.

3.1. Total pressure-oxidation process

The total pressure-oxidation process (King and Dreisinger, 1995; Marsden *et al.*, 2003) uses high-temperature and pressure-oxidation conditions to oxidize all sulfide minerals to sulfates and sulfuric acid followed by direct recovery of copper from diluted autoclave discharge solutions. Conveniently, total pressure-oxidation also results in iron precipitation as hematite (Eq. 11).

King and Dreisinger (1995) studied the total oxidation of chalcopyrite concentrates and found that residence times of 15–30 min were adequate at 220°C for complete (>99%) copper extraction and sulfide oxidation. The total-oxidation process is particularly advantageous for copper–gold ores. Gold can be recovered by direct cyanidation of the washed autoclave solids. Silver, if present, will likely be fixed at least partly as silver jarosite in the autoclave solids. To improve silver recovery, a lime boil is recommended (2 h at 95°C with an excess of CaO). Silver jarosites are decomposed by the lime and silver becomes available for subsequent cyanidation:

$$\begin{aligned} AgFe_3(SO_4)_2(OH)_6 + 2CaO \rightarrow {} & 0.5Ag_2O + Fe_2O_3 \\ & + 2CaSO_4 \cdot 2H_2O + H_2O \end{aligned} \tag{12}$$

The use of total pressure oxidation for chalcopyrite concentrate treatment results in significant oxygen consumption (more than 2 t O_2/t Cu leached) and significant acid production. Acid is produced by the autoclave process. Further amounts of acid are liberated by solvent extraction (SX) of copper. In total, ~3 t of H_2SO_4 are produced per tonne of Cu leached. The cost of initial production of this acid (effectively the very high oxygen consumption) usually requires that this acid be used as a source of *make-up* acid for associated leaching operations. The cost to neutralize this acid would generally be just too high to bear. Alternatively, if this acid can be used beneficially, the acid credit can be significant. For example, at an acid cost (USD) of $80/t, the value of acid from the high-temperature autoclave is effectively 3 × $80 = $240/t Cu leached. This equates to about $0.11/lb of Cu, a very significant credit.

The Phelps Dodge Company has now pioneered the large-scale application of total pressure-oxidation at the Bagdad plant in Arizona (Marsden *et al.*, 2003). At this facility ~16,000 tpa of Cu can be recovered from concentrates that previously were sent to a smelter facility. Under total-oxidation conditions, 140 short tonnes of acid are produced per day for application to the stockpile leach operation at Bagdad. In this way an acid credit is derived.

Fig. 3 shows the flowsheet adopted by Phelps Dodge for the Bagdad plant. A single autoclave is used to leach the concentrates; the discharge then proceeds to flashing (to return the slurry to atmospheric pressure), slurry cooling, CCD washing and then copper SX/EW. The autoclave stream is merged with the stockpile leach solution stream to provide a combined pregnant leach solution (PLS) feed to the SX/EW facility. The acid from the autoclave process is then recycled in the SX raffinate back to the stockpile leach.

The washed autoclave residue is neutralized with lime in four stages. If precious metals were present (there are very low levels of precious metals in the Bagdad concentrate), the neutralized residue could be cyanide-leached.

The total pressure-oxidation process is very suitable for application where the acid from pressure leaching can be used beneficially. The process has been commercially demonstrated at a large scale and could easily be scaled up to

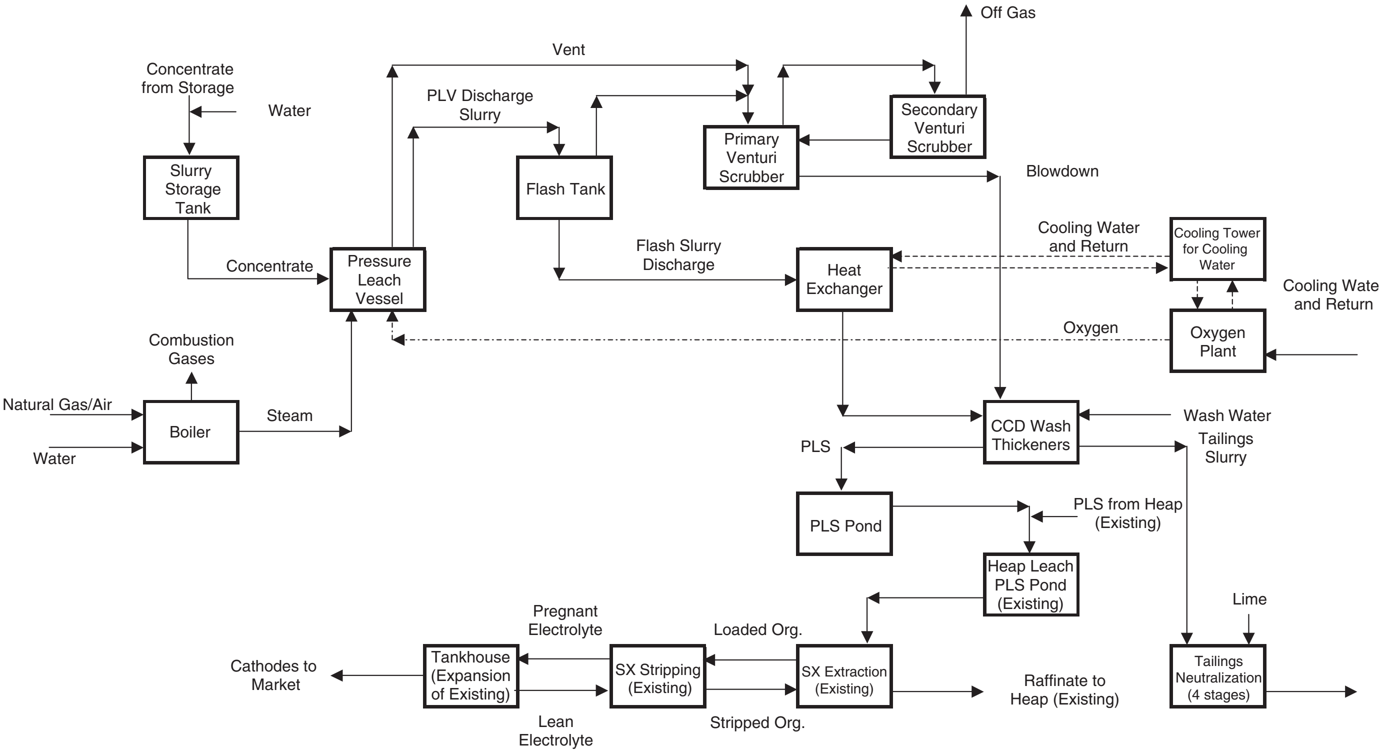

Fig. 3. The Phelps Dodge Total Pressure Oxidation flowsheet (after Marsden *et al.*, 2003).

larger size if required. Total pressure oxidation for copper concentrate treatment should now be regarded as “proven” technology.

3.2. BIOCOP^{TM} process

The BIOCOP^{TM} process was developed by the BHP Billiton biotechnologies group based in Johannesburg South Africa (Dew and Batty, 2003). The process uses thermophile bacteria to oxidize and leach copper from sulfide concentrates. The general process flowsheet is shown in Fig. 4. The thermophile bacteria oxidize sulfide minerals to metal sulfates and sulfuric acid at temperatures of 65–85°C. Thermophile bacteria are superior to mesophile bacteria in the leaching of chalcopyrite concentrates. Mesophile bacteria produce poor copper extractions unless the chalcopyrite is finely ground prior to bioleaching (it is believed that passivation is a problem for leaching of coarse chalcopyrite particles).

The BIOCOP^{TM} flowsheet has a number of interesting features.

- Oxygen is used for bioleaching. This necessitates the provision of an oxygen plant. Previously, bioleach plants for gold and base metal applications were operated with air blowers.
- Arsenic may be removed in a separate step to produce a residue for disposal.
- Copper may be recovered by SX/EW. Excess acid may be used in heap leaching if appropriate.

The Alliance Copper joint venture group (BHP Billiton and Codelco) have now commercialized the process in Chile. A 20,000 tpa Cu plant has been built close to Chuquicamata with the long-term goal of treating arsenical

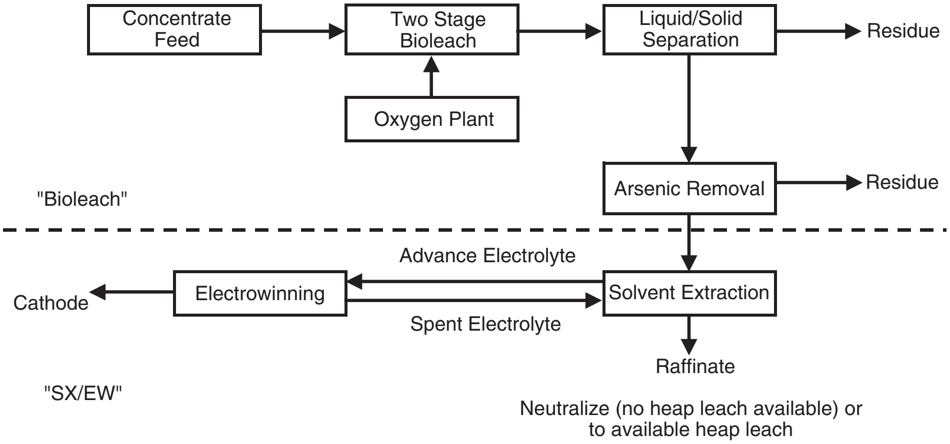

Fig. 4. The BIOCOP^{TM} Process (after Dew and Batty, 2003).

concentrates from the Mansa Mina deposit. The plant is integrated with a copper heap-leach circuit to allow for an acid credit back to the bioleach plant. The BIOCOP^{TM} process is therefore similar to the Total Pressure Oxidation Process described above, in that high copper extractions are achieved under total-oxidation conditions (to sulfates). It is believed that all sulfides/sulfur will be oxidized to sulfate in the leach. The major difference between BIOCOP^{TM} and Total Pressure Oxidation seems to be in the availability of acid after copper SX. In the bioleach process, acid neutralization is practiced in the two-stage bioleach using limestone addition to the bioleach slurry. This neutralization incurs an operating cost that is not present in total oxidation and effectively reduces the available acid credit from the bioleach process. Nevertheless, for specific applications such as high arsenical ores, the bioleach approach may be favoured relative to pressure leaching. Clearly, the successful start-up of the Alliance Copper project in Chile has validated the technology at a significant scale. Bioleaching of copper concentrates is now regarded as a proven technology.

It is expected that for treatment of arsenical copper–gold concentrates a cyanidation circuit for recovery of gold from the bio-oxidation residue would logically be applied. This would be augmented by *lime boil* if justified by lockup of silver in jarosite.

3.3. Outokumpu Hydrocopper^{TM} process

The Outokumpu Hydrocopper^{TM} Process (Hämäläinen *et al.*, 2003) is shown in Fig. 5. The process involves counter-current leaching of chalcopyrite using air and chlorine as oxidants (chlorine oxidizes cuprous to cupric for leaching process). The residue from leaching contains goethite and elemental sulfur. Gold may be leached selectively from the residue under controlled-potential leaching conditions, as the gold-chloride complex. Gold is recovered by adsorption/precipitation on activated carbon or by chemical precipitation.

The copper-bearing solution is purified by pH adjustment to precipitate cupric ion (for recycle to the leach), cementation (aided by soluble mercury salt) for silver removal, base-metal precipitation using sodium carbonate and then finally an ion-exchange process for polishing minor impurities (using C-467 resin from Duolite). The purified cuprous solution is then treated with sodium hydroxide to precipitate hydrated cuprous oxide for hydrogen reduction to metal.

The three major reagents needed for this process are chlorine, sodium hydroxide and hydrogen. These are all produced using a standard chloro-alkali cell. The use of electrochemistry for chemical manufacture, rather than for metal winning, is a major step forward in application of chloride technology. Chloro-alkali cells are typically operated at 3,000–6,000 A/m^2 current

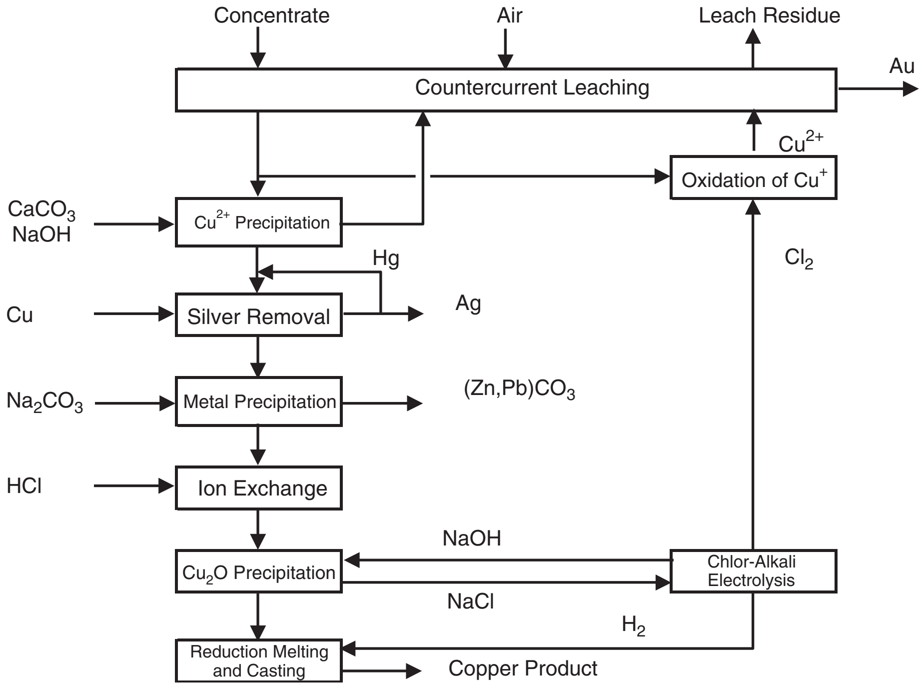

Fig. 5. The Outokumpu Hydrocopper Process (after Hämäläinen *et al.*, 2003).

density, about an order of magnitude higher than conventional metal winning. In addition, anode-to-cathode distances are measured in *mm*, not *cm*, owing to the absence of a metal deposit growing in the electrode gap.

The main reactions (for chalcopyrite leaching) are shown below:*Chalcopyrite leach*:

$$\begin{aligned} &CuFeS_2 + 0.5Cl_2 + 0.75O_2 + NaCl + 0.5H_2O \\ &\qquad \rightarrow NaCuCl_2 + FeO(OH) + 2S \end{aligned} \tag{13}$$

Gold leach:

$$Au + 3CuCl_2 + 4NaCl \rightarrow NaAuCl_4 + 3NaCuCl_2 \tag{14}$$

Copper precipitation:

$$NaCuCl_2 + NaOH = 2NaCl + CuOH\ (s) \tag{15}$$

Copper reduction:

$$CuOH + 0.5H_2\ (g) = Cu + H_2O \tag{16}$$

Chlor-alkali cell:

$$NaCl + H_2O = NaOH + 0.5Cl_2\ (g) + 0.5H_2\ (g) \tag{17}$$

The products from the chloro-alkali cell are exactly balanced with the requirements for copper leaching, purification and copper reduction.

The successful leaching of gold requires a sufficiently high oxidation potential to form the aurichloride complex species. The process does not oxidize pyrite, so only gold that is exposed to solution in the concentrate/leach residue will be recovered by this method. Silver is directly leached into solution as a silver-chloride species and can be recovered by cementation on a mercury-coated copper granule. The mercury coating forms a silver amalgam upon cementation of silver.

Outokumpu have commissioned a ~1 t/d of copper demonstration plant in Finland for this technology.

3.4. Anglo American Corporation/University of British Columbia copper process

The Anglo American Corporation/University of British Columbia (AAC/UBC) Copper Process (Dempsey and Dreisinger, 2003; Dreisinger *et al.*, 2002a) is a medium-temperature leaching process for chalcopyrite concentrates. The concentrate is reground to a fine size (P_{80} of 5–20 μm) and leached under moderate pressure at 150°C in an acid-sulfate system. The addition of a surfactant (lignin sulfonate and/or Quebracho) disperses the molten elemental sulfur, avoiding passivation during leaching. Copper is recovered by SX and EW to produce premium copper cathode. The process is distinguished by high copper extractions, hematite or jarosite formation for iron rejection, and elemental sulfur as the predominant reaction product. Fig. 6 illustrates the importance of grind size for leaching of a chalcopyrite concentrate. For all except the 17.93 μm particle size, copper extraction exceeded 95% at a 2 h autoclave leaching time. At a coarser particle size, copper extraction stopped at about 80% due to passivation of coarse chalcopyrite particles in the feed.

The Anglo American Corporation/University of British Columbia process was evaluated in a continuous, fully integrated pilot-plant trial (Dreisinger *et al.*, 2003). The flowsheet (see Fig. 7) comprised fine grinding of the concentrate, pressure leaching, thickening and filtration, copper SX/EW, with a bleed circuit to recover valuable base metal co-products. Gold and silver were recovered from the autoclave residue by direct cyanidation. Copper and zinc extractions above 95% and elemental sulfur yields of 60% were achieved at 150°C in a 2 h residence time. The presence of surfactants did not affect the extraction or the phase separation in the SX process. The gold extraction from the washed residue was reported in two tests at 82.1 and 84.1%. Silver extraction was 21 and 21.8% for the two tests (owing to presence of silver jarosite in the autoclave solids). Very high reagent consumptions were reported, at 13.1–24.4 kg/t NaCN and 37.3–37.8 kg/t $Ca(OH)_2$.

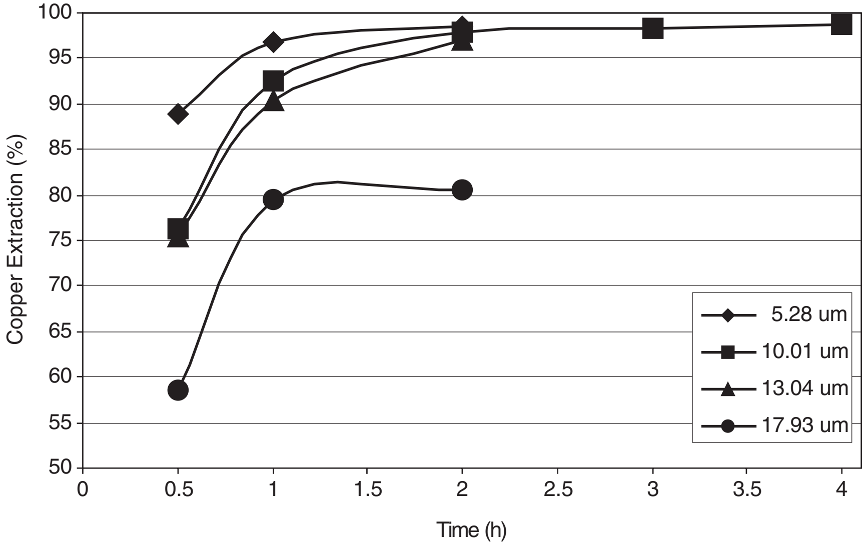

Fig. 6. Copper extraction as a function of initial particle size for leaching of chalcopyrite concentrate with surfactant addition at 150°C (after Dreisinger *et al.*, 2002a).

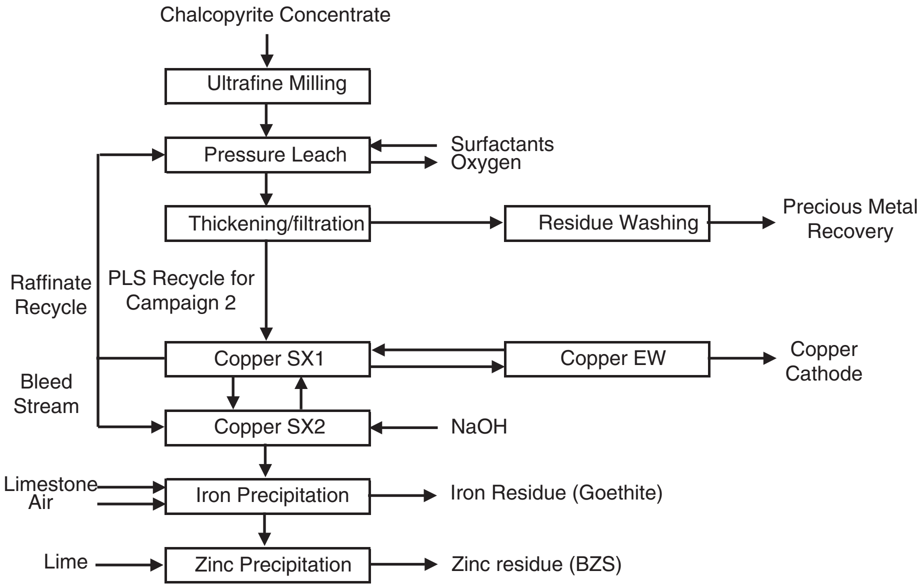

Fig. 7. Pilot-plant flowsheet for the Anglo American Corporation/University of British Columbia Copper Process (after Dreisinger *et al.*, 2003).

The consumption of NaCN was largely due to formation of NaSCN in the cyanidation, with a minor contribution from formation of copper and zinc cyanide complexes:

$$\mathrm{NaCN + S \rightarrow NaSCN} \tag{18}$$

The consumption of lime is due to reaction with elemental sulfur (and perhaps sulfates) in the oxidation residue. The *lime-sulfur* reaction is shown below, with formation of thiosulfate and *penta*sulfide ion at high pH:

$$\mathrm{3CaO + 12S \rightarrow CaS_2O_3 + 2CaS_5} \tag{19}$$

The gold and silver extraction results are unfortunately representative of 'direct' cyanidation of elemental sulfur-containing autoclave residues. Gold recovery is often poor due to locking in unoxidized sulfides, sulfur coating or the presence of coarse gold (sometimes formed by over-milling of concentrate to improve reactivity). Silver losses to jarosite are routinely encountered. Finally, the two reactions for consumption of cyanide and lime result in a significant economic penalty to the precious metal recovery process (not to mention the environmental challenges posed by formation of large concentrations of thiocyanate and thiosalts). All sulfate-based processes that result in formation of elemental sulfur in the copper-leach residue face similar challenges in precious-metals recovery.

A number of alternative methods for precious-metal recovery from elemental sulfur-containing residues have had historical and current interest. Thiosulfate leaching is a natural process for consideration (Berezowsky and Gormely, 1978) given that thiosulfate can be formed by simple addition of lime to the residues (see Eq. (19)). It is also believed that halide leaching (chloride or bromide or a combination) or acid-thiocyanate or thiourea leaching might be preferred alternatives to cyanide for these materials. These reagents offer the possibility of lower overall cost (as sulfur reactions are much reduced compared to lime/cyanide). Further work is required to develop and test these technologies. See Chapters 21 and 22 for more detailed discussion of these options.

3.5. PLATSOL® process

The PLATSOL® process (Fleming *et al.*, 2001), which utilizes addition of small amount of chloride salts to the *total oxidation* autoclave leach to cause the precious metals to dissolve at the same time as the sulfide minerals are oxidized, was developed for the treatment of ore from the NorthMet property (formerly called Dunka Road) in Minnesota, USA, owned by PolyMet Mining Corporation of Denver, Colorado. This process is covered in detail in Chapters 35 and 36. The following discussion considers the application of the process to copper–gold ores.

The PGMs, which include platinum, palladium, rhodium, ruthenium, osmium and iridium, typically occur in nature in close association with base metals sulfides, such as those of copper and nickel. Gold, although not traditionally included as one of the PGMs, is also frequently found in these ore bodies in varying concentrations. There are a number of situations in which it is undesirable or uneconomic to treat gold and PGM concentrates by the conventional route. In these situations, direct oxidative pressure leaching of a concentrate to dissolve the base metals may provide the best process economics. As with matte leaching, gold and the PGMs remain in the pressure-leach residue.

3.5.1. Application to copper–gold ores

The PLATSOL® process may also offer a non-cyanide process treatment option for recovery of copper and gold from copper–gold and gold–copper concentrates. Ferron *et al.* (2002) reported on batch laboratory testing of a copper–gold concentrate and a refractory gold–silver concentrate under PLATSOL® conditions. The results are presented in Table 2. Clearly the use of this process permits high overall extractions of copper, gold and silver. It is interesting that the formation of silver jarosite is prevented due to complexation of silver by the chloride present in the autoclave leach liquor.

A potential flowsheet for copper–gold ores may comprise an initial base-metal recovery step, followed by a PLATSOL® treatment to recover any remaining base metals as well as precious metals (see Fig. 8). If elemental sulfur is formed during the base-metal leaching step, then it would be advantageous to remove at least a portion of this sulfur prior to the PLATSOL® leach step. This could possibly be done by a variety of methods including flotation and hot filtration of sulfur.

4. CONCLUSIONS

The hydrometallurgical treatment of copper and copper–gold concentrates using chemical and biological leaching has begun to make inroads to the field

Table 2
Chemical analyses of refractory concentrates and PLATSOL® extraction results

Concentrate	Chemical analysis				Extraction (%)		
	Cu (%)	S (%)	Au (g/t)	Ag (g/t)	Cu	Au	Ag
Cu–Au	28.9	33.3	5.7		99.7	95.9	
Au–Ag			19.9	19.4		96.0	99.5

Source: (after Ferron *et al.*, 2002).

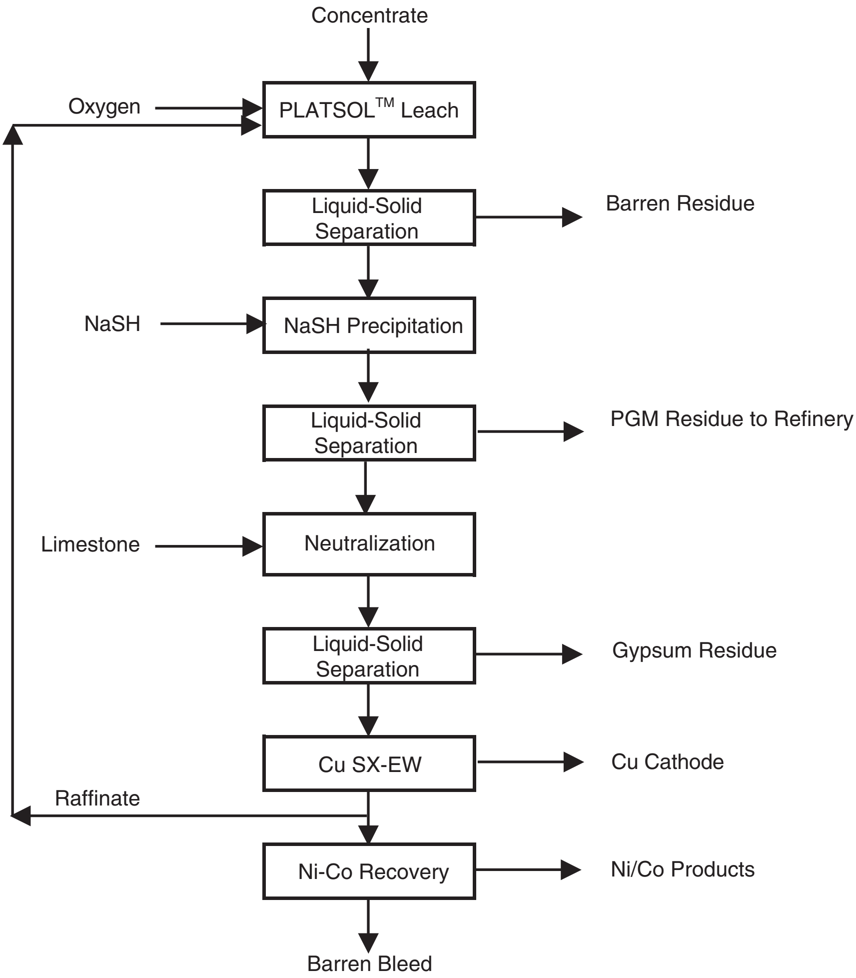

Fig. 8. Simplified PLATSOL® flowsheet for copper–gold ores.

traditionally dominated by smelting and refining. The field has tended to advance thus far by necessity or unique opportunity. The Mt. Gordon and Sepon processes were developed to recover copper from ores that were not easily amenable to conventional flotation. The total pressure-oxidation process has been commercialized by Phelps Dodge; the acid from the total-oxidation autoclave can be beneficially used in the stockpile-leach process at Bagdad, Arizona. The BIOCOP™ process has been applied at a unique opportunity at the Chuquicamata complex in Chile. Copper concentrates containing high arsenic concentrations, which are not easily treated through a smelter, will be treated through the commercial bioleach plant with by-product weak-acid solutions used for associated heap-leaching operations.

The AAC–UBC and PLATSOL® processes may have potential for selected applications, including copper and copper–gold concentrate treatment. The AAC–UBC process niche appears to be a situation where partial oxidation of sulfur to sulfate is desirable. This may be attractive where a modest quantity of acid can be used in an associated heap-leach operation or where the cost of acid neutralization is low and economically feasible. If acid can be used on a heap leach, a small acid credit would then be applied back to the concentrate treatment process.

It is predicted that further niche applications of hydrometallurgy for concentrate treatment will continue into the future. However, the industry is still waiting for a technology that can compete on an operating cost/capital cost and metal recovery basis with the conventional smelting/refining process. The difficulty with all sulfate-based processes appears to be the oxidation of some elemental sulfur to sulfate during leaching. The cost associated with the sulfur oxidation process and then the process of sulfate control (*e.g.*, neutralization), makes it difficult to achieve a low operating cost for copper production, except where the acid is used to offset an existing acid consumption for an associated heap leach. The recovery of precious metals from sulfate-based process residues can also be challenging. The cyanidation recovery of gold and silver from a residue containing elemental sulfur and silver jarosite is difficult due to consumption of cyanide and lime by reaction with elemental sulfur and poor silver extraction due to refractory silver jarosite.

The chloride processes for concentrate treatment offer some promise in meeting the challenge of conventional smelting and refining technologies. Chloride processes are attractive due to rapid copper leaching, high solution strength, very low sulfur to sulfate oxidation and low temperature/atmospheric pressure operation. The INTEC process continues to be developed for copper concentrate treatment. The most challenging step for INTEC is the use of EW for metal recovery. Formation and recovery of copper metal dendrites by deposition in the INTEC EW cell can be difficult. The Outokumpu Hydrocopper process has the attraction of use of electrochemistry for reagent synthesis (chlorine/hydrogen and sodium hydroxide). It is significant that Hydrocopper is able to extract and recover gold from copper–gold concentrates using selective gold leaching in strong brine solutions.

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Chapter 34

Processing of high-silver gold ores

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1. INTRODUCTION

There are a numerous gold deposits where the recovered silver grade exceeds that of the recovered gold grade so that silver output in terms of metal produced exceeds that of gold. However, at current metal prices, silver production needs to be more than about 70 times that of gold to be of greater economic importance.

This chapter deals principally with ores where the silver grade is sufficiently high to warrant modification to the design of the plant relative to that which would be specified if the silver component was not present, and where the silver and gold are amenable to recovery by conventional cyanidation, refractory ores being dealt with in Section III.2.

2. FUNDAMENTALS

Gold and silver occur together in the alloy electrum, which has no fixed composition although the term is frequently applied to minerals with more than 20% silver. Minor quantities of copper, iron and bismuth are frequently present.

Native silver is found in nature. Other minerals that tend to be cyanide soluble and of economic significance include chlorargyrite [AgCl] also known as cerargyrite, acanthite [Ag_2S], sometimes incorrectly referred to as argentite, and tetrahedrite [$(Cu,Fe,Ag,Zn)_{12}Sb_4S_{13}$]. Acanthite in particular tends

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to dissolve slowly, requiring an excess of cyanide (McQuiston, 1985), while iodargyrite [AgI] is reported to have dissolved very rapidly at Pajingo in Queensland (Bax, 2004).

There are over 200 argentiferous mineral species and identification of which ones are present is an essential component of designing a treatment route to optimize silver recovery.

Metallic silver dissolves anodically in aqueous cyanide solution, in a similar manner to gold, in line with the following reaction (Marsden and House, 1992):

$$Ag(CN)_2^- + e = Ag + 2CN^- \text{ subind} : (E^\circ = -0.31 \text{ V}) \quad (1)$$

The *E*h–pH diagram for the Ag–CN–H_2O system, given in Fig. 1, shows the region of predominance of $Ag(CN)_2^-$ and indicates that insoluble silver cyanide, AgCN, is formed at low pH. The area of predominance of AgCN (s) is sensitive to the cyanide concentration; however, cyanide levels prevalent in gold-leaching processes are well in excess of those under which such an insoluble species would form (Caruso, 1975).

The corresponding cathodic reaction has been shown to be the four-electron mechanism given in Eq. (2) rather than the two-electron path for gold, given in Eq. (3) (Hiskey and Sanchez, 1990):

$$O_2 + 2H_2O + 4e = 4OH^- \ (E^\circ = 0.401 \text{ V}) \quad (2)$$

$$O_2 + 2H^+ + 2e = H_2O_2 \ (E^\circ = 0.69 - 0.059\text{pH} - 0.095\text{pO}_2 \text{ V}) \quad (3)$$

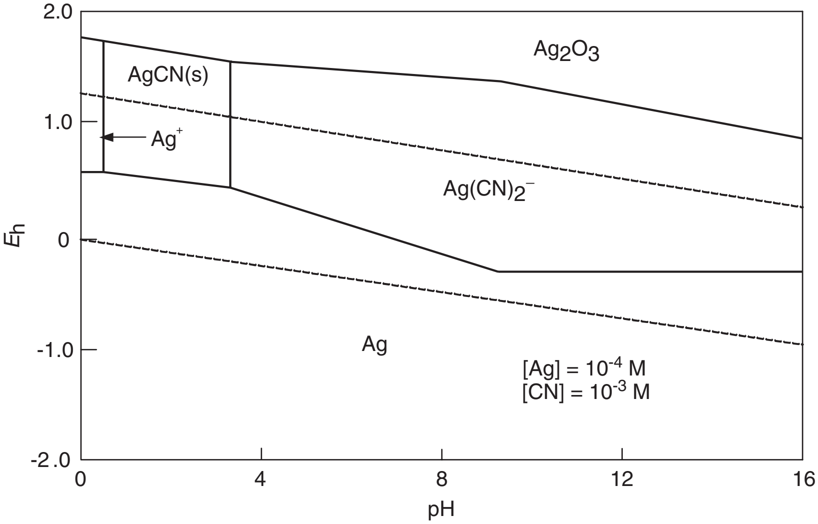

Fig. 1. *E*h–pH diagram for the Ag–CN–H_2O system at 25°C (after Osseo–Asare *et al.*, 1984).

For conditions typically prevailing in gold leaching, the dissolution rate for silver is slower than for gold. This is illustrated in the current–potential curves given in Fig. 2, where it can be seen that the difference in dissolution rates, as indicated by the dissolution current density i_d, will be reduced as the cyanide concentration is increased, thus confirming that high-silver ores are frequently beneficially leached at higher cyanide levels.

Table 1 gives the equilibrium constant for Eq. (1), and for the corresponding equilibria for other cyanide complexes (Wang and Forssberg, 1990). This indicates that silver forms one of the intermediate/weaker cyanide complexes, which also mitigates towards the use of higher cyanide strength solutions if significant revenue is to be derived from silver recovery.

Silver loads onto carbon more slowly than gold but elutes and electrowins more rapidly. Costello *et al.* (1988) give considerable evidence of this based on operational data from a number of Australian process plants. The effect of the presence of elevated silver levels on carbon-in-pulp (CIP) or carbon-in-leach (CIL) operation was to reduce the rate of gold loading and stage efficiency to the extent that it was considered that an additional carbon stage was required if significant silver was present. Examples of carbon loading profiles from operating plants indicated that it is not unusual to see gold displacing silver in the first carbon adsorption vessel.

As silver elutes ahead of gold it would be expected to have little effect on the design of the elution circuit. However, the data in Table 2 indicate

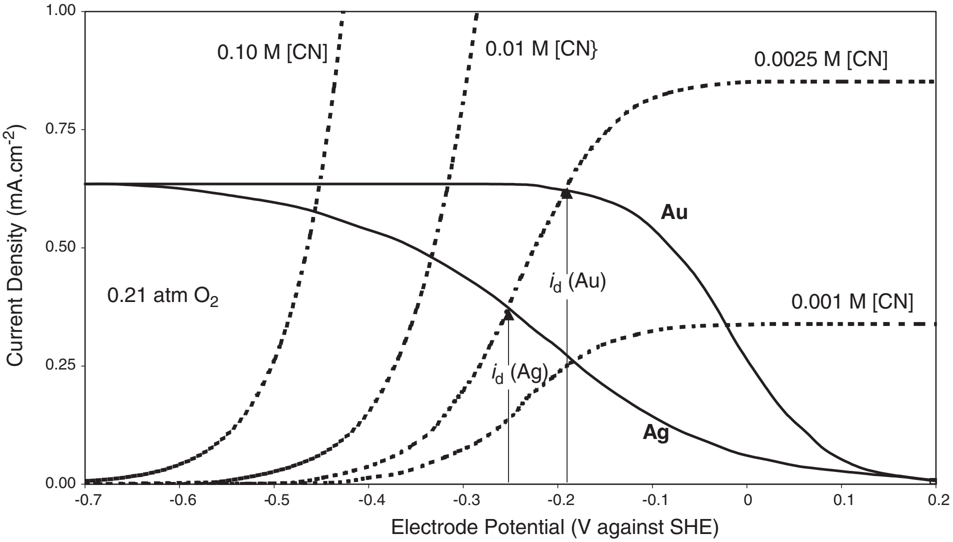

Fig. 2. Electrochemical data for the anodic oxidation of silver and gold and the cathodic reduction of O_2 on silver and gold calculated according to mixed kinetic models (after Hiskey and Sanchez, 1990).

Table 1
Equilibrium constants for cyanide complexes

Cyanide complex	log β_n
$Cu(CN)_2^-$	16.3
$Cd(CN)_4^{2-}$	17.9
$Co(CN)_6^{4-}$	19.1
$Zn(CN)_4^{2-}$	19.6
$Ag(CN)_2^-$	20.5
$Cu(CN)_3^{2-}$	21.7
$Cu(CN)_4^{3-}$	23.1
$Ni(CN)_4^{2-}$	30.2
$Fe(CN)_6^{4-}$	35.4
$Au(CN)_2^-$	39.3
$Fe(CN)_6^{3-}$	43.6
$Au(CN)_4^-$	56.0

After Wang and Forssberg (1990).

Table 2
Silver elution efficiency (%) under various conditions

Elution temp (°C)	Sodium cyanide dosing level (kg/t)			
	10	20	30	Mean
100	59	69	66	65
110	83	79	63	75
120	86	79	72	76
130	93	86	72	84

After Davidson (1985).

enhanced silver recoveries at higher elution temperatures for the Anglo-American Research Laboratories (AARL) elution process.

The base data from which this table is constructed was derived at the AARL in Johannesburg and is therefore primarily determined under circumstances related to Witwatersrand ores, which are low in silver (typically about 10% of the gold level). The extent to which these percentages hold for higher initial carbon loadings of silver is not known, but it is suspected that there may be a tendency towards a constant residual grade on stripped carbon for given elution conditions. Consequently, the recovery differences indicated in the table may be somewhat reduced for higher initial silver loadings. This may be due to the formation of AgCl or metallic Ag on the carbon after hydrochloric acid washing and cyanide-free elution (Adams, 1992).

It is notable that both the Waihi plant (Martha Mine) in New Zealand and the Gunung Pongkor plant in Indonesia were built with 110°C AARL elution circuits and have evidently operated without major difficulty in that area.

Pilot elution testwork (Costello, 2004) has been completed on carbon samples having gold loadings of 700 g/t and silver loadings of 11,000 g/t. The data clearly showed that at these levels of silver the elution efficiency was inversely proportional to the temperature in the range 90–130°C, as shown in Table 3 and 4.

Similar testwork carried out using the same pilot plant on carbon samples having initial loadings of 1,200 g/t Au and 1,005 g/t Ag again demonstrated that silver elution efficiency was inversely proportional to temperature.

Solution elution profiles were sharper and earlier for silver at higher temperatures. It is suggested that at significant silver loadings the lower stability of the silver cyanide complex causes the cyanide complex to decompose and either metallic silver or silver chloride to precipitate, before elution is completed.

The presence of silver will have a significant impact on electrowinning circuit design due to both the increased metal concentration in the eluate solution and the lower atomic weight of silver. The deposit formed is substantially less coherent than for low-silver ores and the most practical way of operating is to use stainless-steel wool for the cathodes and to remove the electrowon deposit with high-pressure water sprays.

Table 3
Pilot-plant results for silver elution efficiency from carbon loaded with 700 g/t Au and 11,000 g/t Ag

Elution temperature (°C)	Elution efficiency (%)
90	87
110	76
120	62
125	61
130	44

Table 4
Pilot-plant results for silver elution efficiency from carbon loaded with 1,200 g/t Au and 1,005 g/t Ag

Elution temperature (°C)	Elution efficiency (%)
110	94
120	92
140	89

In Merrill–Crowe recovery circuits, the presence of silver only impacts on the process to the extent of increasing the amount of zinc dust to be added, and the amount of filter cake that then needs to be handled and smelted.

3. FLOWSHEET SELECTION

3.1. Heap leaching

For the treatment of heap-leach solutions, financial analysis of the process options is relatively straightforward (see Chapter 19). The main process alternatives are Merrill–Crowe and carbon adsorption, although resin adsorption may also be considered with the Connemara Mine in Zimbabwe having operated a resin process for a number of years.

Moolman *et al.* (1983) carried out a comparison of these options and also evaluated a solvent-extraction metal-recovery route. They concluded that the capital and operating costs of carbon adsorption and Merrill–Crowe processes were similar but that operating costs would tend to favour Merrill–Crowe for solution tenors above 5 mg/L gold. They did not specifically consider high-silver ores, but it is not unreasonable to assume that a similar relativity would be maintained on the basis of the concentration of total gold and silver in solution rather than just gold. It is also suggested that most ores producing a liquor tenor of 5 g/t gold would in most cases be most economically treated by leaching of ground slurry rather than by heap leaching.

It is therefore reasonable to conclude that the clear justification to favour Merrill–Crowe over carbon adsorption will normally only occur for high-silver ores where the solution concentration of metal to be recovered is high, but the value of it is insufficient to justify stirred-tank leaching.

The cut off level of 5 mg/L derived by Moolman *et al.* (1985) was made some years ago and will need to be re-evaluated in the light of current metal prices and the cost structure prevailing in the location of the planned project.

The Connemara plant in Zimbabwe operated successfully using a resin process to recover gold, principally because of the low value of base metal and other impurities in the pregnant solution, resulting in a simple and inexpensive elution process being possible at ambient temperature and pressure. Resin technology for gold adsorption resins has progressed since the Connemara plant was built in 1994 and may be worth evaluating for high-silver solutions. Chapter 25 describes this technology in more detail.

3.2. Slurry processes

For ores where it is economic to sustain the additional costs associated with grinding the ore in order to obtain higher recoveries, the situation is generally more complex and difficult to reduce to a simple metal solution grade above which Merrill–Crowe is preferred and below which CIL/CIP is more economic. The range of processes open for consideration is, however, similar to that heap leaching, with carbon absorption, Merrill–Crowe and possibly resin adsorption being the main candidates.

The ease of solid/liquid separation and washing is critical to process economics and there may be external factors that heavily influence process selection.

Examples of high-silver ores where such considerations were relevant include Golden Cross in New Zealand where the high-clay content of the ore meant that the slurry would not thicken beyond an underflow density of 30%, making counter-current decantation (CCD) washing very expensive to implement. At El Peñón in Chile an environmental requirement to dispose of the tailings as a filter cake made the consideration of any process other than Merrill–Crowe uneconomic.

Broad parameters indicated by Costello *et al.* (1988) are that for ores with less than 50 g/t cyanide-soluble silver, CIL/CIP is preferred while Merrill–Crowe will be more economic if cyanide-soluble silver is over 100 g/t. Within the range 50–100 g/t a site-specific evaluation is required. In common with the criteria from Moolman *et al.* (1985) for heap leaching, this yardstick was proposed some time ago and needs to be used judiciously in light of prevailing costs and metal prices.

3.3. Leaching

Depending on mineralogy, the leaching time for the silver component can be longer than for gold. If Merrill–Crowe metal recovery is used this has little impact on the configuration of the leaching circuit, but for carbon recovery will tend to mitigate towards the use of CIP or hybrid CIL rather than pure CIL tank arrangements.

3.4. Gold recovery on carbon

A frequent argument used against the use of carbon adsorption plants for high-silver ores is that the slurry dilution associated with the carbon advance reduces the efficiency of the adsorption process. This is readily overcome by discharging the carbon advance stream onto a sieve bend and returning the slurry to the tank it came from, as was done at Gunung Pongkor in Indonesia, which has a design head grade of 15 g/t Au and 200 g/t Ag.

One of the difficulties with the design of carbon adsorption circuits for high-silver gold ores is that standard adsorption models cannot adequately handle high-silver loadings. In particular, models do not seem able to replicate the displacement of silver on carbon by gold, which is frequently observed in the first contactor of CIP/CIL trains with high metal loadings on carbon.

Adsorption circuit design is therefore best guided by experience from other operations. The conclusion of Costello *et al.* (1988) is that six stages of carbon contacting can be effective provided that the total gold plus silver loading on carbon is limited to 8,000 g/t. Plants have successfully operated at higher loadings than this, an example being Gunung Ponkor, which was designed on 15,000 g/t Au + Ag loaded carbon; however, it is suggested that detailed operating data are required from an operation with similar Au/Ag ratio and solution tenors before attempting to replicate its performance.

Elution of carbon is most frequently by the AARL process. Pressure Zadra has been used successfully on high-silver ores, for example at Temora, New South Wales, but it is felt that the sensitivity to gold returning to the column in the initial spent electrolyte and the lack of flexibility in throughput tends to favour the AARL approach (Costello *et al.*, 1988). Although plants have successfully operated with elutions at 110°C, it is most common to design an elution circuit that is capable of operating at 120–130°C. This means that separate columns are required for elution and acid washing because the butyl rubber lining frequently used in AARL columns is not suitable at these temperatures.

At Misima Mines in Papua New Guinea the AARL elution was run at two temperature levels to provide two eluates: one high-gold low-silver and the other low-gold high-silver (Zandee, 1993).

Following elution, gold and silver can be recovered from the eluate by electrowinning, continuous zinc cementation or batch zinc cementation. Electrowinning becomes labour-intensive as the silver content rises, but it is difficult to define a crossover point at which zinc cementation becomes more economic. As previously noted, silver tends to be electrowon ahead of gold and consequently any underperformance of the electrowinning circuit is likely to have a higher impact on gold recovery.

Zinc precipitation from eluates should not require deaeration as oxygen should be removed from the eluate as part of the cyanide degradation reaction, which will occur at elevated temperature in contact with carbon during the elution.

Frequently zinc dust is added on a continuous basis as the eluate leaves the elution circuit. An alternative used at Golden Cross in New Zealand was to upflow the eluate into a large conical-bottomed batch tank to minimize air entrainment, add zinc dust and any other chemicals, such as cyanide or lead nitrate, required to give optimum precipitation conditions, and then pump the tank out through a filter press.

This gives good control over the precipitation reaction and minimizes the amount of zinc remaining in the filter cake, eliminating the need for acid washing.

After removal of excess zinc in a sulfuric acid leach, Misima used a nitric-acid leach to dissolve the silver, which was then precipitated with sodium chloride and smelted. This resulted in a high-silver bullion containing only 2% gold and a high-gold bullion containing 50–70% Au (Zandee, 1993).

3.5. Gold recovery by Merrill–Crowe

A typical block flow diagram for a plant treating a high-silver gold ore by Merrill–Crowe metal recovery is given in Fig. 3.

The thickening stage following grinding may not be essential, in which case the clarification section is fed only with the pregnant liquor from the solid/liquid separation and washing stage.

Solid/liquid separation and washing is most commonly carried out in a CCD circuit, but horizontal-belt vacuum filtration with multiple washing stages can also be used. Filtration steps for clarification and separation of the zinc precipitate are normally carried out in plate-and-frame filter presses.

The amount of metal handled in the gold room of a plant treating high-silver ores can become quite considerable to the extent of justifying the use of a reverbatory furnace for smelting and use of a custom mould producing ingots of more than 100 kg in mass.

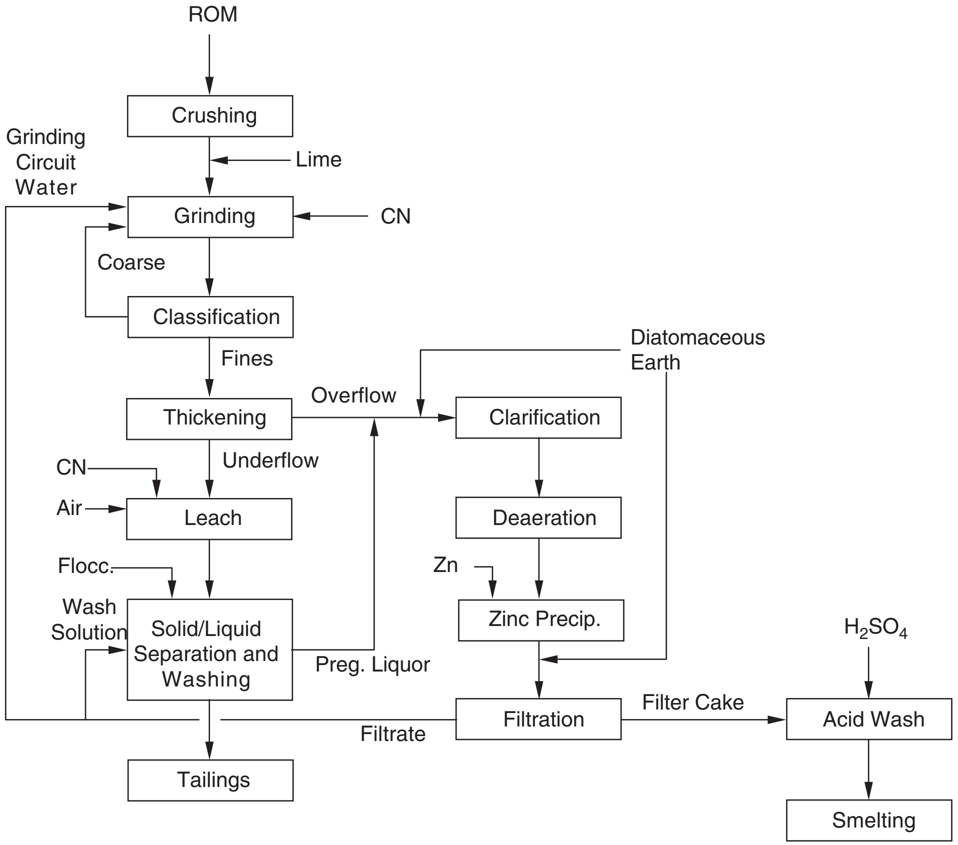

Fig. 3. Typical Merrill–Crowe flowsheet.

4. INDICATIVE PLANT DESIGN CRITERIA

Typical design criteria are given here for the unit operations associated with high-silver gold ore plants. The Merrill–Crowe criteria will be similar whether this style of plant is installed on a heap leach or stirred-tank leach and is dealt with under the latter category.

Heap leach (carbon adsorption):

Number of carbon contactors:	4 or 5
Solution flux in contactors:	$61\,\mathrm{m^3/m^2/h}$ for 60% bed expansion
Carbon bed expansion:	50–60%
Carbon used:	6/16#
Carbon loading:	14,000 g/t (Au + Ag) or 2,600 x (Au + Ag) solution grade, whichever is lower.
Carbon per contactor:	1–2 x elution batch size.

Carbon adsorption:

Number of carbon contactors:	Minimum 6.
Carbon loading:	8,000 g/t (Au + Ag) or 1,300 x (Au + Ag) solution grade, whichever is lower.
Carbon per contactor:	1–2 x elution batch size.
Elution type:	AARL at 120–130°C.
Electrowinning current efficiency:	10%.

Merrill–Crowe

Clarifier filter duty:	This will be ore dependent but typical duties are in the region of $2.5\,\mathrm{m^3/m^2/h}$ at inlet pressures up to 7 bar. Diatomaceous earth pre-coat is normally required.
De-aeration vacuum:	>75 kPa vacuum.
Dissolved oxygen level:	<1 ppm.
Zinc precipitation filter duty:	$1.25\,\mathrm{m^3/m^2/h}$ with diatomaceous earth pre-coat at inlet pressures up to 7 bar. Filter feed pump should have a submerged gland to prevent air ingress.
Zinc precipitate:	Typically contains Zn 7–10%. SiO_2 10–15%, moisture 30%.

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Mike Costello is thanked for the supply of pilot-plant data and reference material. Some of the information used in this chapter is derived from material that has not been formally published, but is a consequence of the author either having carried out the process design for the plants personally or having been the Metallurgical Manager of the engineering company that executed the design. These plants include, Waihi, Gunung Pongkor, Connemara, Golden Cross and El Peñón.

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Chapter 35

Recovery of gold as by-product from the base-metals industries

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1. INTRODUCTION

Although most of the gold produced each year originates from primary gold ores or concentrates, a significant amount of gold is recovered as by-product from the production of base metals and from the recycling of scrap.

From a current gold world production of approximately 2,600 tonnes, about 10% is recovered as a by-product (Chen and Dutrizac, 2004). Most of it is recovered as a by-product from the copper industry, but significant quantities of gold are also recovered as a by-product from the nickel and lead industry, and the potential also exists to recover gold as a by-product from the zinc and cobalt industry.

This chapter discusses the recovery of gold as a by-product from copper smelters and from the other base metal industries. There are often platinum-group metals (PGMs) that are also recovered as a component of the by-product; more detailed discussion of gold recovery with PGMs may be found in Chapter 36, although Section 7 summarizes some direct leaching processes for precious metals (PMs).

The current chapter will focus on commercially applied processes, while also considering proposed new processes and emerging technologies.

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2. RECOVERY OF GOLD IN COPPER SMELTERS

Previous chapters in this book (32 and 33; see also 12) deal with the recovery of gold from copper ores at the mine-site.

Gold is often associated with chalcopyrite in ore deposits, and efforts are therefore obviously made at the mine to maximize the recovery of both gold and copper, either using a combination of gravity and flotation techniques, or flotation alone. Using available techniques, some of the gold can be recovered directly as a gold concentrate, using, for example, gravity techniques in the grinding circuit, but usually, significant quantities remain within the copper concentrate.

Gold can be present in the copper concentrate as free gold particles or in solid solution in the chalcopyrite itself. For example, at Norilsk, the chalcopyrite has been measured to contain between 1 and 7 g/t of Au in solid solution (Sluzhenkin and Mikhov, 2003).

During the smelting operation, gold, silver and other PMs remain closely associated with copper, first within the matte and then within the blister. Finally, during electrorefining of the copper blister, gold is concentrated and collected with the anode slimes.

The composition of anodic slimes varies from smelter to smelter, depending on the types of feeds and the operation. Table 1 presents typical compositions of copper anodes and anode slimes from some Canadian refineries.

During the smelting of copper concentrates, gold and other PMs are almost quantitatively collected within copper. In the blister anodes, gold is exclusively present in solid solution. Most of the copper in the anode

Table 1
Typical compositions of Canadian commercial copper anodes and anode slimes (after Chen and Dutrizac, 2004)

Element	Copper anodes (g/t)	Anode slimes (% m/m)
Cu	98.9–99.2%	16–24
Au	10–100	0.1–2.0
Ag	350–2,000	4–25
Se	340–1,200	4–15
Te	10–290	0.2–3.5
As	100–600	0.5–2.0
Sb	10–220	0.3–2.0
Bi	5–75	0.1–0.8
Pb	300–1,700	4–22
Ni	1,800–5,500	0.4–26
O	1,400–2,500	–

dissolves during electrorefining and approximately 5–10 kg of anode slimes are produced per ton of anode. In those slimes, gold has been released as tiny ($<1\,\mu m$) metallic Au particles which settle at the bottom of the cells, to be eventually embedded in a matrix of copper sulfate and a complex oxidate phase of a Cu–Ag–As–S–O composition. Close association of gold with an Ag–Cu selenide phase appears probable.

Anodic slimes contain significant amounts of copper, lead, silver, selenium, nickel and tellurium, and various smelters have over the years elaborated a multitude of schemes to separate gold from all the other components in the slimes.

Various examples are presented in the following sections of processes used to recover gold from copper anodic slimes. Most copper concentrates also contain small, but not insignificant, quantities of PGMs. These eventually find their way, together with gold and silver, into the copper refinery anodic slimes (see Chapter 36). Most large copper refineries, therefore, normally operate a precious-metal (PM) plant where anodic slimes are treated. The process used can vary from plant to plant.

2.1. Noranda CCR refinery

In 1998, Noranda CCR Division commissioned a new anode slimes treatment plant (Lessard, 1989; Bilodeau *et al.*, 1987; Morrison, 1985; 1989). Before that time, the plant process was as illustrated in Fig. 1.

The process to recover gold from the Moebius cell mud had remained largely unchanged since the 1930s. Disadvantages of this process included a high (30%) circulating load of Pd through the acid leach of gold mud from the Moebius cell, and significant gold in-process inventory. A new process, developed at the Noranda Research Centre, has been installed to overcome these problems. A simplified process flowsheet of the new installation is illustrated in Fig. 2.

The incoming gold mud typically assays 45% Au, 35% Ag, 14.2% Pd, 1.5% Cu and 0.5% Pt. The new process generates 99.99% Au, and 90% Ag cement for recycling to the Doré furnace, and a Pd/Pt concentrate assaying 90.8% Pd, 3.2% Pt, 2% Cu, 1.35% Pb and 0.66% Se. In 1988, the silver refinery produced 801 t of silver bullion, 26.6 t of gold and 3.85 t of Pd/Pt concentrate.

2.2. The Outokumpu Pori refinery

The process used at Pori (Hyvärinen *et al.*, 1984) is summarized in Fig. 3.

The electrolyte slimes undergo a series of stages: decopperizing by oxidative leach followed by filtration; nickel removal by pressure leaching at 160°C; selenium removal from the slimes, followed by Doré smelting of the resulting slimes; electrolytic silver refining in a Moebius cell; gold mud is further purified (H_2SO_4 leach) then dissolved in *aqua regia*; gold is recovered

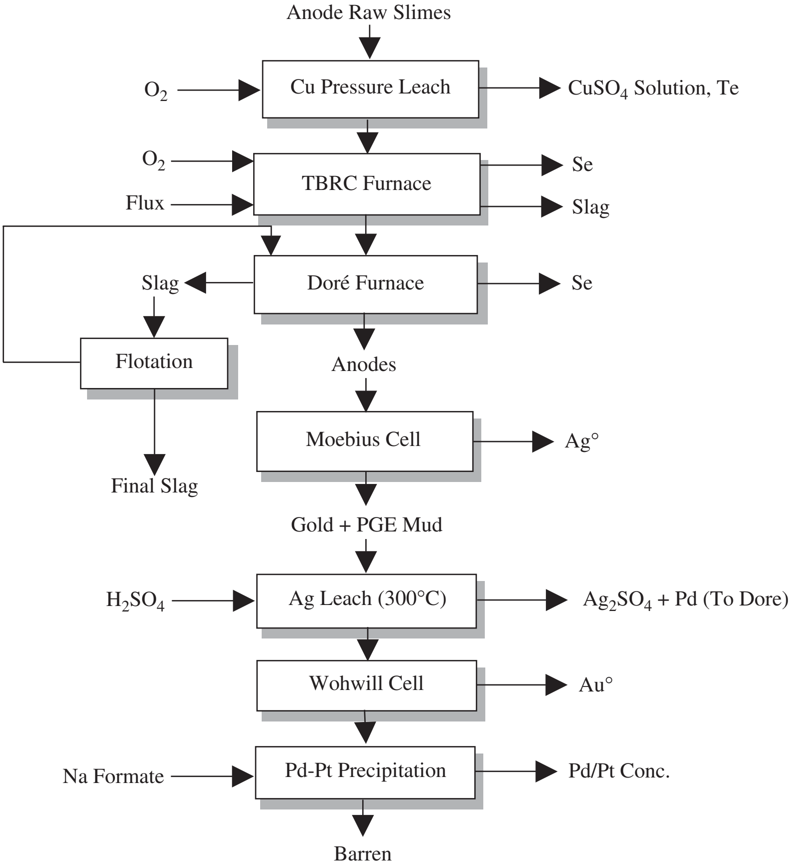

Fig. 1. CCR anode slimes treatment plant in 1988.

from the solution by reduction (Na_2SO_3); and PGMs are cemented with iron to produce a 45% Pt, 45% Pd sponge.

In 1983, Outokumpu Pori refinery produced 38 t of silver, 1.1 t of gold, and 2000 kg of Pt/Pd sponge (45% Pt, 45% Pd).

2.3. Phelps Dodge El Paso refinery

The new refinery recently commissioned to treat Phelps Dodge's anodic slimes has been described in detail (Hoffmann and Wesstrom, 1994). The process is illustrated in a simplified form in Fig. 4. This is a very elegant process based on an early separation of the silver (the main constituent) from the rest of the PMs, and gold solvent extraction (SX). The silver-leaching step

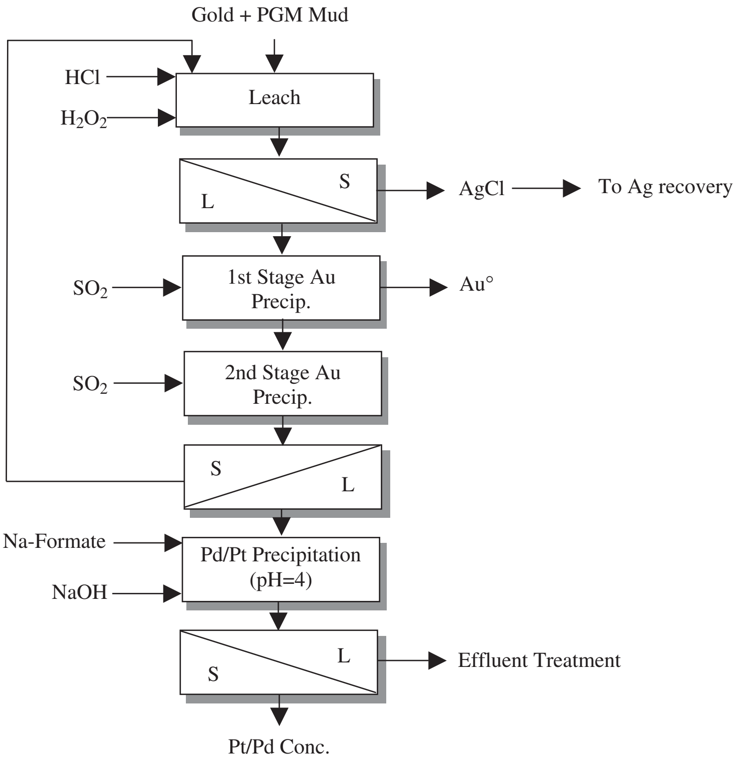

Fig. 2. New hydrometallurgical process to treat CCR anode slimes (simplified).

is based on the metathesis reaction:

$$Ag_2SO_4 + Ca(NO_3)_2 \rightarrow 2AgNO_3 + CaSO_4 \qquad (1)$$

The calcium nitrate is produced by reacting hydrated lime to consume nitric acid generated at the anode, as per the reaction

$$2HNO_3 + Ca(OH)_2 \rightarrow Ca(NO_3)_2 + 2H_2O \qquad (2)$$

Moreover, gold is separated from the remainder of the precious metals (PGMs) using SX.

Very pure products are achieved using this new process, 99.95% and 99.995% for silver and gold, respectively. After 2 years of operation, Phelps Dodge refinery was producing 3.1 M troy oz Ag, 86.000 troy oz Au, 2,000 troy oz Pd and 200 troy oz Pt.

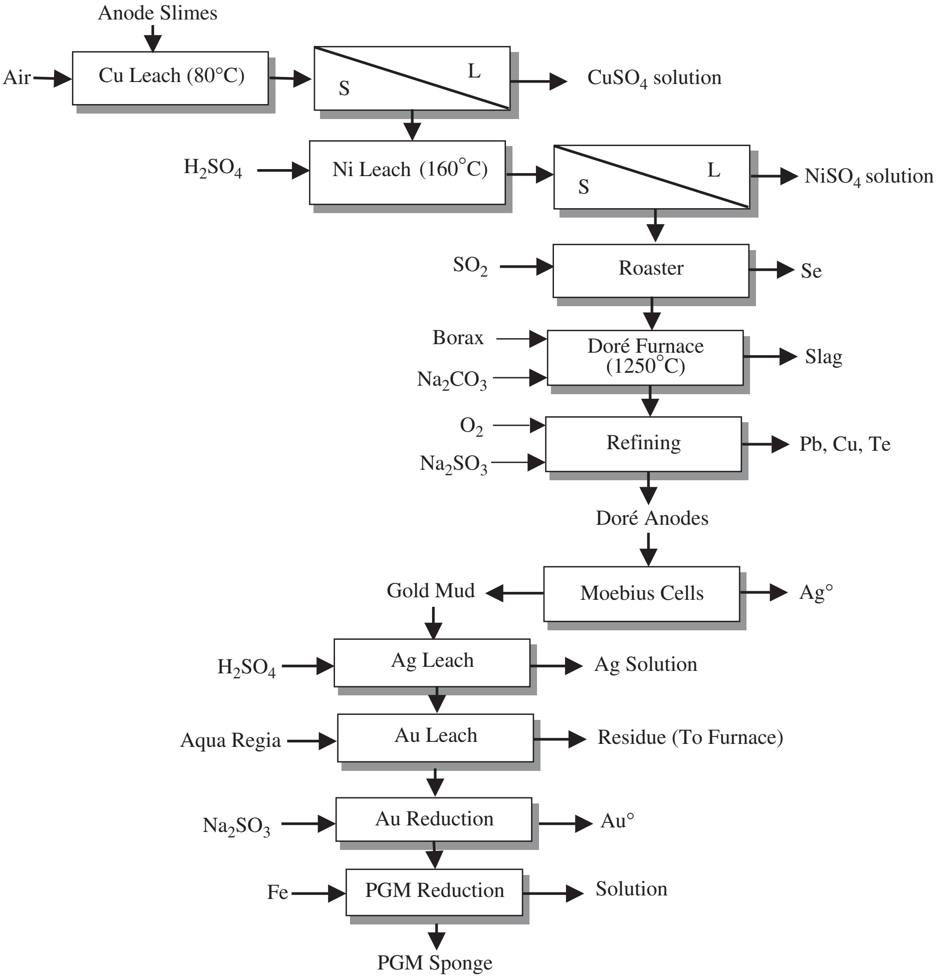

Fig. 3. Precious metals refining process used at Outokumpu Pori refinery.

3. RECOVERY OF GOLD AS A BY-PRODUCT FROM NICKEL SULFIDE ORES

The main nickel-bearing sulfide mineral, pentlandite [$(Fe,Ni)_9S_8$] is normally recovered by froth flotation from large deposits in Norilsk (Commonwealth of Independent States), Sudbury (Canada) and Western Australia.

Some of these nickel deposits can contain significant PGMs (Merensky Reef, UG-2 Reef in South Africa, Norilsk), but gold is also found as a minor constituent in these ores.

In the Merensky Reef ores, gold is found almost exclusively as metallic gold or electrum [Au_xAg_y] and is almost always associated with the

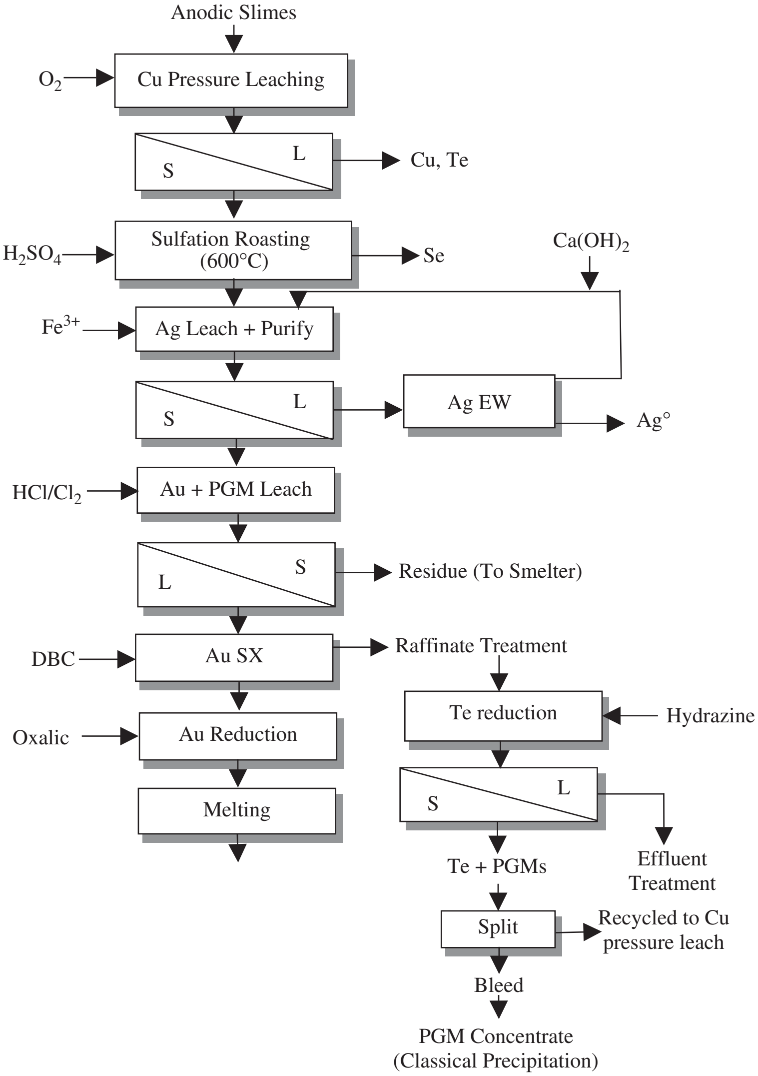

Fig. 4. Simplified process flowsheet for Phelps Dodge Slimes Refinery.

chalcopyrite [$CuFeS_2$] also present in these ores (Vermaak and Hendricks, 1976). In Norilsk ores, gold mineralization is also associated with the sulfides, with higher gold grades in the disseminated ore type than in the massive ore type (Sluzhenkin and Mikhov, 2003). Here too, the main gold carrier is electrum with varying Au/Ag ratios. The gold–silver alloys form 2–3 μm rims at the surfaces of PGM minerals and chalcopyrite. In both cases, gold is also present as an alloy with palladium and other elements such as Pt, Cu, Pb, Sn.

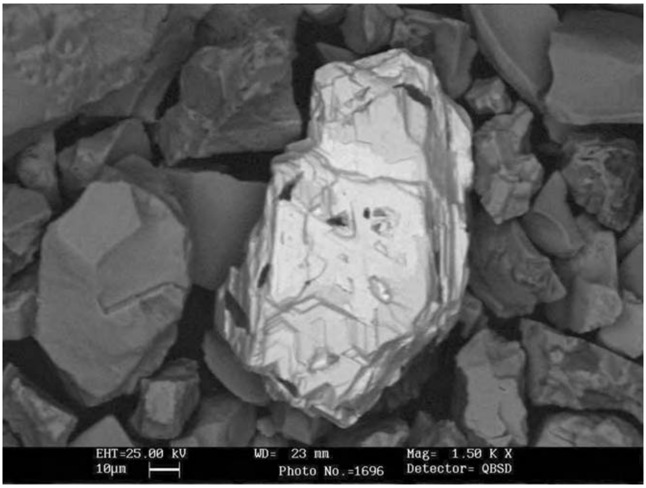

Fig. 5. Pd-PGM grain coated with Au at the Lac des Isles deposit (courtesy of Hamilton, 2004).

Palladium–gold associations are also identified in other deposits, such as the Lac des Isles deposit in Ontario (Canada), as shown in Fig. 5 (Hamilton, 2004).

Depending on the relative ratio of nickel and precious metals in a concentrate, it will be processed in a nickel or a precious-metal smelter. The recovery of gold from PGM concentrates is discussed in Chapter 36. In the following sections, examples of the PMs recovery from the nickel ores for the three major nickel producers in the world are presented (Cole and Ferron, 2002).

3.1. Inco

The Inco process for the treatment of its Sudbury ores has been well described (Wiseman *et al.*, 1988; Tyroler *et al.*, 1988). Fig. 6 summarizes the process and indicates how the high-grade PGM concentrates are produced.

Starting from a low PGM grade (~1 g/t PGM) in the mixed ore, Inco produces refined nickel and copper and by-product precious metal concentrates, as anode slimes and carbonyl process residues. The residue from the carbonyl process assays 55–60% Cu, 6–10% Ni, 4–8% Co, 4–9% Fe, 13–19% S, 600–900 g/t (Au + PGM) and 750–1350 g/t Ag. It is treated in a two-stage pressure leaching process to dissolve first the nickel and the cobalt, and then the copper + selenium + tellurium. PGM concentrate from the nickel circuit contains 60–80% (PGM + Au), plus some silver and a variety of base metals such as tellurium, antimony, tin, lead, bismuth, copper, nickel and iron. Concentrate from the copper circuit is largely palladium and

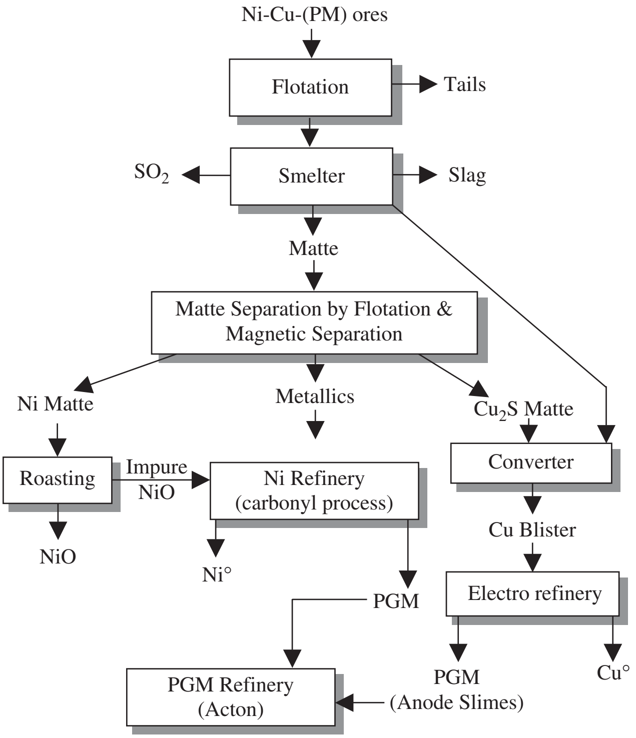

Fig. 6. Recovery of PGMs during Inco's treatment of Sudbury ores.

platinum, with some rhodium, and generally much less base metals than the concentrate from the nickel anode slimes. These concentrates are refined in Inco's Acton refinery in the UK.

The final refining step consists of transforming the high-grade PM concentrate into high-purity (>99%) individual elements (Pt, Pd, Ir, Os, Ru, Rh), as well as recovering the gold and silver accompanying the PGMs. Several papers describing the chemistry and principles underlying the refining of the PGMs have been published (Edwards, 1976; Demopoulos, 1989; Foo, 1982). The success of the classical refining step is based on manipulating, both from a thermodynamic and kinetic point of view, the complex aqueous chloride chemistry of the PMs; the methods developed many years ago to extract, separate and refine the various PMs are based on analytical chemistry principles. The classical process circuit was initially developed to treat electrolytic slimes; it is rather complex and is, in practice, based on *aqua regia* solubilization followed by successive steps of salt precipitation and redissolution, followed by thermal reduction to metal.

The classical refining process used for many decades by Inco at its Acton refinery in the UK is illustrated in simplified form in Fig. 7. Details have been

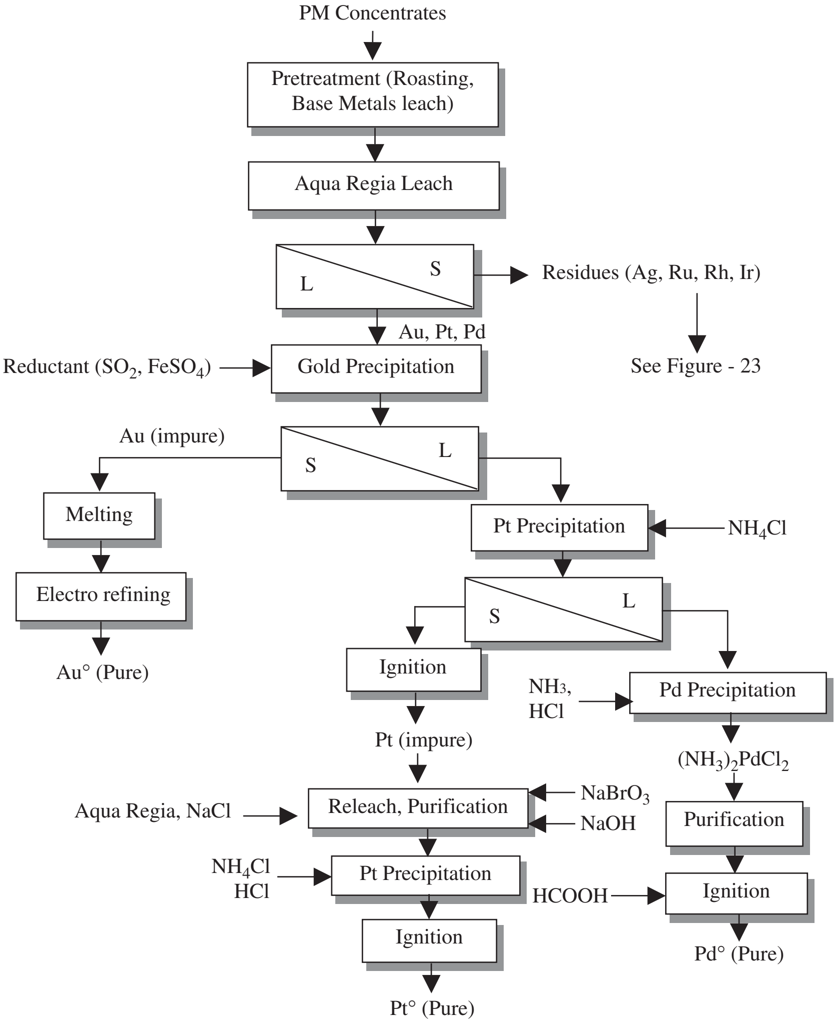

Fig. 7. Classical refining process for Au, Pt, Pd – Inco Acton Refinery.

published elsewhere (Demopoulos, 1989). In a very simplified form, the classical process previously used at Acton can be described as *aqua regia* dissolution of Au, Pt, Pd; and gold recovery from solution by reduction.

The process described in Fig 7 has been used for decades and is still in use, partly or totally, in various locations. It is rather complicated, however; it gives a poor first-time yield of refined metals and requires lengthy refining times (up to 6 months for rhodium!). It also results in significant in-process inventory of PGMs, affecting the overall economics of PGM refining because of the high cash value of the metals held up.

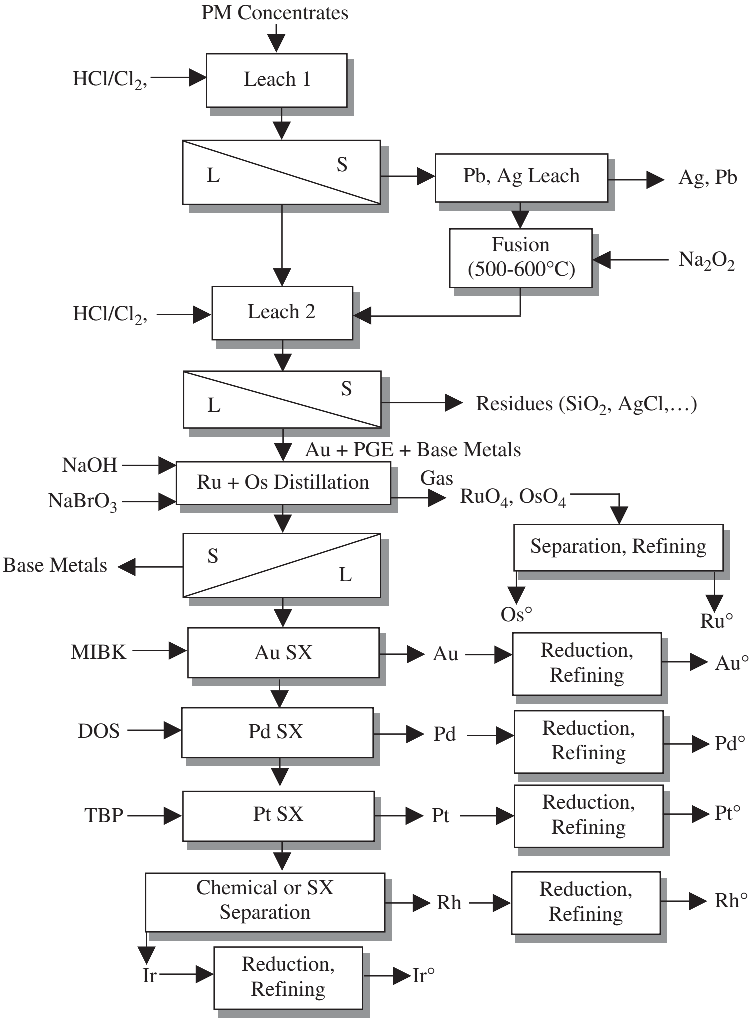

Fig. 8. Modern refining process scheme (simplified) at Inco, Acton, UK.

Because of the factors described above, the industry was forced to introduce new separation technologies, namely SX. Due to the selectivity and efficiency of the SX process, several refineries have opted for a total leach approach followed by a sequential metal separation with the aid of SX.

The process used at Acton by Inco is presented in a simplified form in Fig. 8 (Barnes and Edwards, 1982): gold SX was introduced first in 1971 and, following its successful application, work was undertaken to investigate the applicability of SX to the separation of the other precious metals in solution.

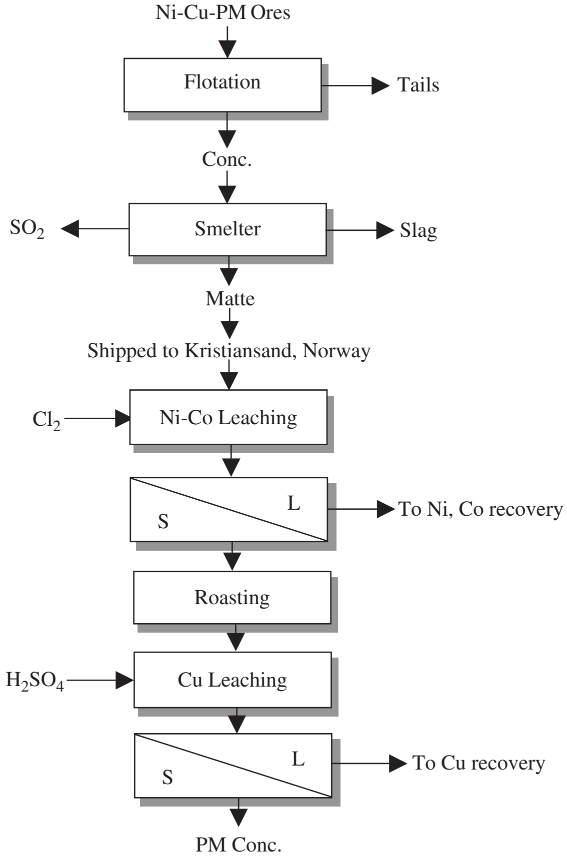

Fig. 9. Falconbridge chlorine process to recover Ni, Cu, Co and PMs.

3.2. Falconbridge

Falconbridge in Sudbury treats ores similar to Inco's but the approach to recover base metals and the PMs is completely different (Hougen and Zachariasen, 1975; Stensholt *et al.*, 1986, 1988, 2001). The Falconbridge process for the recovery of PMs from ores is presented in a simplified form in Fig. 9.

The nickel and the cobalt are fully recovered to pure metals from a chloride system; the copper is roasted to form sulfates and is recovered conventionally from sulfate solutions. The PMs are concentrated in the sulfuric acid leach residue. The residue is reduced to metal using hydrogen, and leached with chlorine under controlled redox potential to minimize the dissolution of PMs. The solid residue is the primary PM concentrate; it is smelted to matte in an electric furnace; the matte is granulated and leached with HCl/Cl_2 to obtain the final PM product.

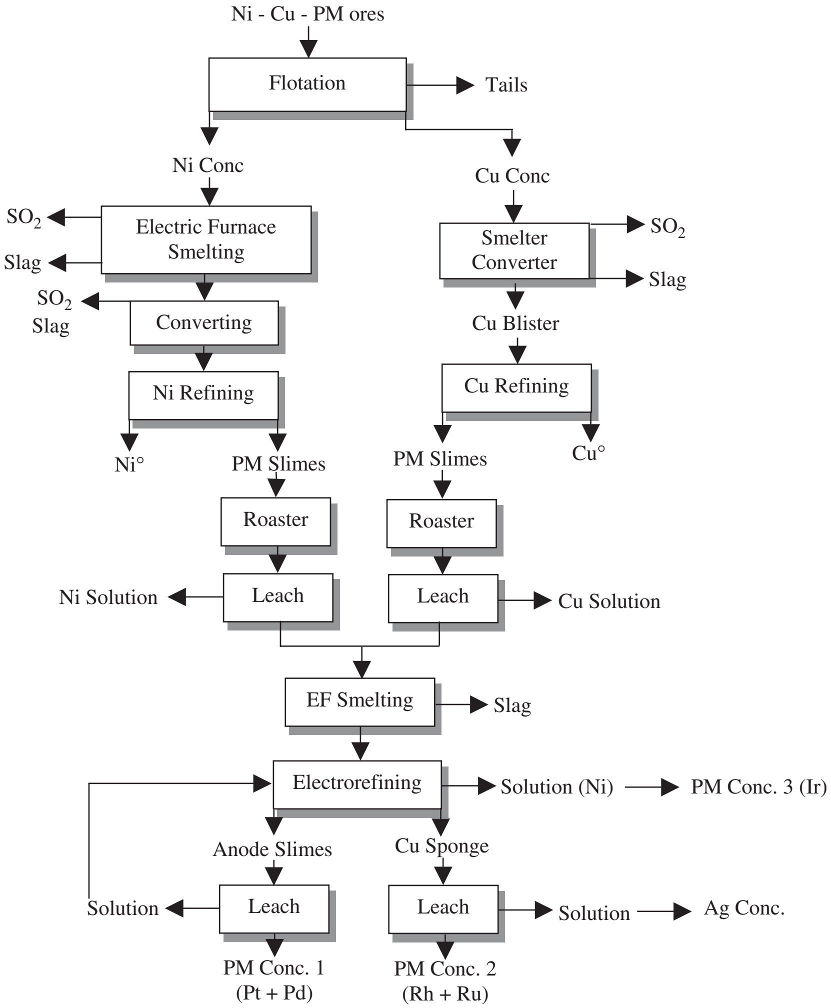

Fig. 10. Norilsk Complex – existing refining process (simplified).

3.3. Norilsk

The Mining and Metallurgical Company, Norilsk Nickel (MMC Norilsk Nickel), is one of the largest producers of nickel and PGMs in the world. Norilsk has operated a metallurgical complex to treat its ores for many years. The present process is illustrated in Fig. 10, as described recently (Ter-Oganesyants *et al.*, 2000). The PGMs are recovered in the anodic slimes from both the nickel and the copper circuits. The slimes are roasted and leached separately to recover the nickel and the copper, respectively; the leach residues are then combined in an electric furnace, wherefrom anodes are electrorefined; the anode slimes are leached in sulfuric acid to generate a PGM concentrate

No. 1 containing 60%–65% (Pt + Pd); the spongy copper precipitate is also leached in sulfuric acid to generate a PGM concentrate No. 2, containing 2.5%–3.5% (Rh + Ru); finally, the spent electrolyte, containing mainly nickel sulfate, is treated to precipitate a PGM concentrate No. 3 assaying 10–20% Ir. This process recovers higher than 99% of the major PGMs (Pt + Pd), but it has a long processing cycle for the slimes (30 days), a large amount of material in progress, and is not very flexible for processing other PGM feed materials.

A new process, developed in-house by Norilsk Nickel to overcome the shortcomings of the present operation and make use of the most modern technology,

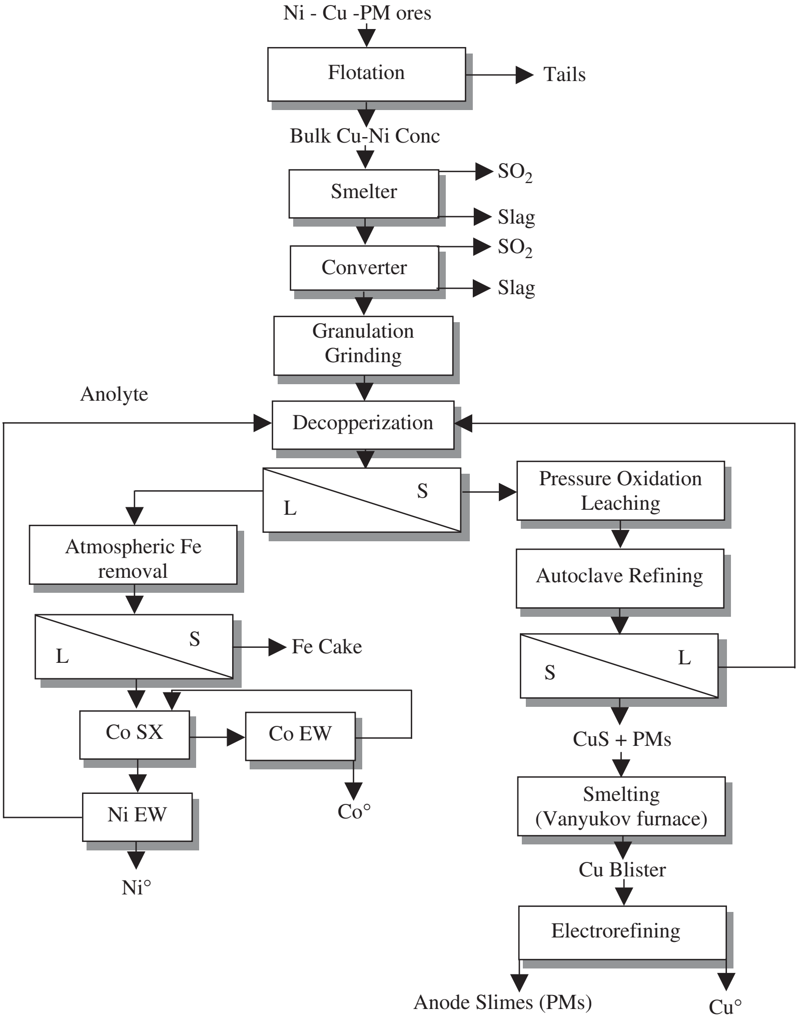

Fig. 11. Norilsk Complex – proposed new base-metals refining process (simplified).

is given in Fig. 11. (Shestakova *et al.*, 2000). Several major modifications are being incorporated at the flotation plant, the smelter and the base-metals refinery. At the flotation plant, a bulk Cu–Ni concentrate will be produced, and a new mill is now being constructed by Outokumpu Oy on behalf of Norilsk.

At the smelter, a high-copper converter matte would be produced, with a copper-to-nickel ratio of about 2:1; the matte would be granulated, wet-ground, and then treated in the new base-metal refinery that would be using a new sulfuric acid leaching technology composed of

- an atmospheric decopperization process whereby matte is used to decopperize the nickel anolyte;
- atmospheric iron hydrolysis using nickel or sodium carbonate (under oxidizing conditions); and
- an oxidizing pressure leaching stage, followed by autoclave refining of the copper concentrate.

The acid-leaching technology maintains the sulfur balance by treating a bleed of the nickel anolyte with sodium carbonate to produce nickel carbonate and a sodium sulfate effluent.

This new process would result in a copper concentrate containing all of the copper (70%–71% Cu grade), little iron (0.2%–0.6% Fe), little nickel (0.4%–0.7% Ni), (26%–28% S) and practically all of the PGMs (in addition to gold). This concentrate would be autogeneously smelted in Vanyukov furnaces to copper blister at the Nadezhda smelter and the PMs recovered in the anode slimes during electrorefining of the copper blister. A simplified flow diagram of the new enrichment process is illustrated in Fig. 11.

Significant improvements would also be incorporated in the new PGM refinery:

1. Pressure leaching would be used to process both the copper and the nickel anode slimes.
2. Refinery wastes (rich in Rh), used catalysts and gravity concentrates would also be treated in separate lines.
3. All resulting PGM concentrates would be blended and smelted to matte in a Kaldo furnace.
4. The resulting matte would be pressure-leached, and eventually will produce a silver concentrate (AgCl), a PGM concentrate No. 1 (Pt + Pd) as leach residue, as well as a PGM concentrate No. 2, by precipitation with thiourea and refining to 35% (Rh + Ru + Ir).

With this process, the slimes processing cycle would be reduced to 4 days. A simplified flow diagram of the new PGE refinery is presented in Fig. 12.

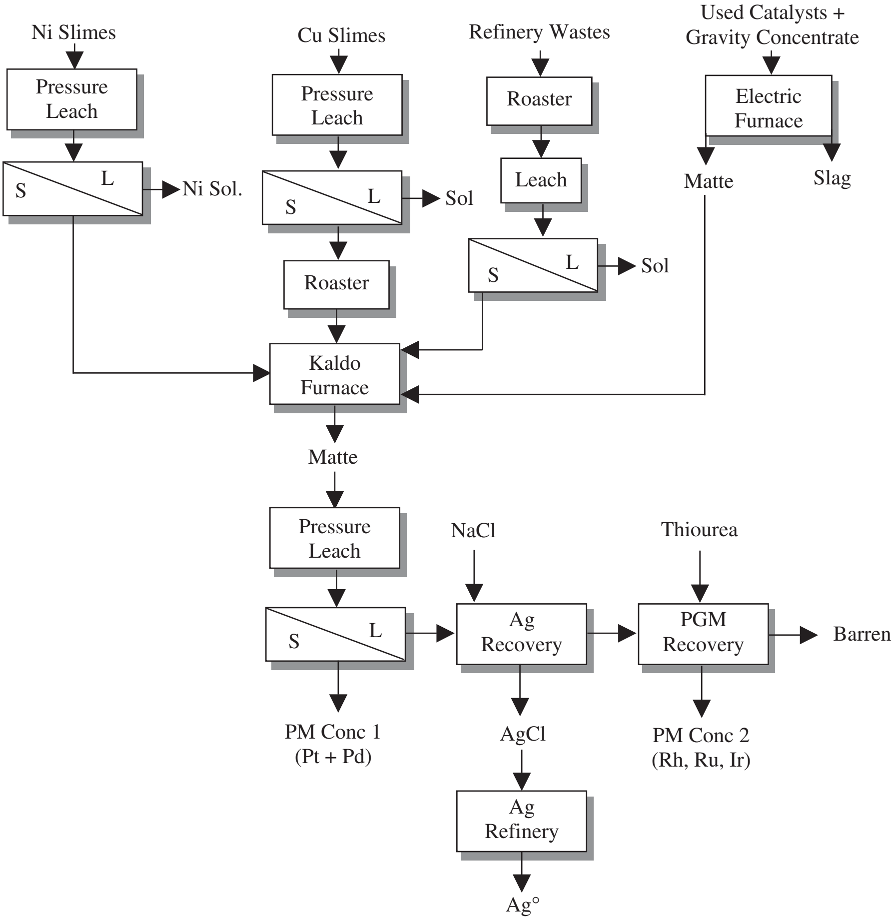

Fig. 12. Norilsk Complex – proposed new PM recovery process (simplified).

4. RECOVERY OF GOLD IN ZINC SMELTERS

Gold is sometimes found in association with sphalerite [(Zn,Fe)S], although the association is rather rare. When the mineralogy is favourable and the concentration of gold warrants it, the possibility of separating gold from the zinc at the concentrator is real. One such example is given by Minera El Toqui in Chile (*Anon*, 1993).

At Minera El Toqui, the zinc ore from the Doña Rosa mine assays 9% Zn and 1.93 g/t Au, with the gold associated with lead. A lead-gold pre-float prior to the zinc flotation allowed the mine to recover 7,100 oz of gold in 1992, in a concentrate assaying 71 g/t Au. In general, however, the gold grade and the mineralogy do not allow the separation of gold from the zinc at the mine and gold is incorporated within the zinc concentrate, or is left behind with the pyrite, as is the case at the Olympias mine in Greece. Typical zinc concentrates assay a few tenths of a gram per tonne of gold.

Zinc metal is won from zinc sulfide concentrates via a variety of processes, some pyrometallurgical, but mostly hydrometallurgical.

4.1. Roast-leach-electrowinning

The most commonly used process, the so-called roast-leach-electrowinning (RLE) process, does concentrate the PMs in one stream, as illustrated in Fig. 13.

Gold and silver in the original concentrate accumulate in the leach residue, together with the lead. Due to the mass losses during roasting and leaching, the PM content of the leach residue is increased several fold. As an example, gold and silver in the Brunswick Mining and Smelting zinc concentrate increases from 0.3–0.4 g/t Au and 70–120 g/t Ag in the calcine to 1-1.5 g/t Au and 200–360 g/t Ag in a pH 2–3 leach residue (Rosato *et al.*, 1990).

Processes have been developed to recover silver and gold when the value of these elements in the leach residue warrants it.

At the Balen plant of Vieille Montagne in Belgium, the hot-acid leach residues are being floated to selectively recover first a silver–gold concentrate using a standard sulfide promoter, followed by lead sulfate flotation using a laurylamine or sulfonate collector (Ek, 1989; Bodson, 1976). A thiourea leach process was also developed to treat the PM concentrate.

At the Iijima Refinery of Akita Zinc Co., treating a zinc concentate assaying 1.2 g/t Au and 186 g/t Ag, more than 98% of the gold reports to the leach residue ('Cu-Pb-Ag residue') that assays 10.9 g/t Au and 1,587 g/t Ag. The leach residue then undergoes a flotation step whereby a Cu–Au–Ag concentrate is produced that assays 19.1 g/t Au and 2,267 g/t Ag, with recoveries of 82% and 85% for gold and silver, respectively (Onozaki *et al.*, 1990).

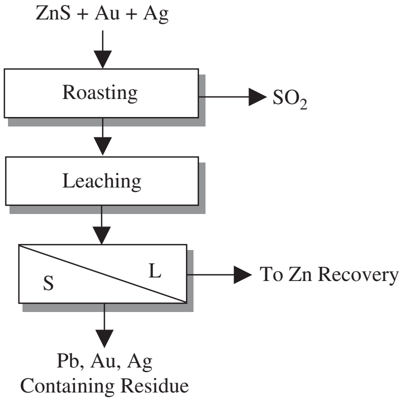

Fig. 13. Precious metals deportment during the RLE Process (simplified).

Leach residues are also floated at the Zhuzhou Smelter in Hunan, China, (Huang, 1990) and sulfidization flotation has also shown promise (Rastas *et al.*, 1990).

Direct leaching of the zinc leach residue has also been proposed, and various lixiviants have been suggested, such as cyanide and thiourea (Ek, 1990).

Leaching of a zinc residue assaying 20–23% Zn, 1–1.5 g/t Au, 200–360 g/t Ag and 4–9% Pb in 4 g/L thiourea resulted in 85–95% Ag and 65% Au extractions in 15 min at 75°C. Carbon-in-pulp was used to extract gold and silver from the solution. After elution with thiourea–butanol and cementation with zinc dust, the final PM concentrate assayed 45% Cu, 30% Ag, 0.4% Au. The process was piloted at a scale of 1 t/d of calcine by Noranda (Rosato *et al.*, 1990).

Another approach to recover gold and silver from jarosite leach residues from the zinc industry was proposed by Tecnicas Reunidas of Spain; in the Plint process, summarized in Fig. 14, the leach residue is submitted to an acidic chlorination leach, with chlorine added to solubilize the gold. After solid–liquid separation and iron precipitation, gold and silver can be cemented using Zn powder; the zinc chloride solution is then processed to metal using the TR electrowinning cell (Frías *et al.*, 2000; Frías *et al.*, 2002).

4.2. Sherritt Gordon zinc pressure-leaching (ZPL)

Dynatec (formerly Sherritt Gordon) has developed a zinc pressure-leach process to directly leach sphalerite [(Zn, Fe)S] without prior roasting. Several commercial installations have been operated successfully for many years.

The process can be simply described as illustrated in Fig. 15.

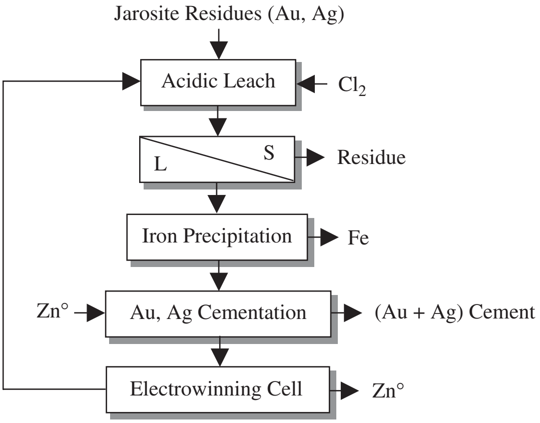

Fig. 14. Plint process to recovery gold and silver from jarosite residues.

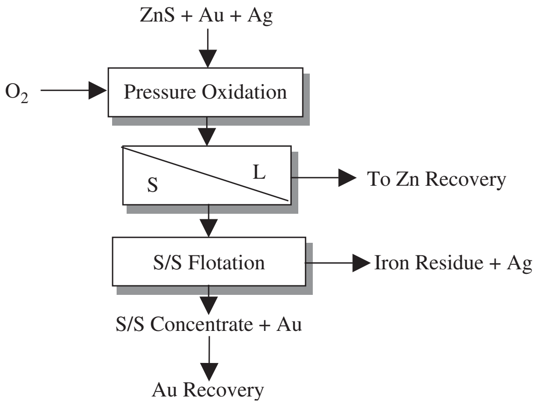

Fig. 15. Sherritt ZPL process (simplified).

The overall process chemistry can be represented as

$$ZnS + 1/2O_2 + H_2SO_4 \rightarrow ZnSO_4 + H_2O + S^\circ \tag{3}$$

Compared to the RLE process, the leach residue contains Au, Ag and elemental sulfur.

The pressure-leach residue can be further treated by floating the elemental sulfur and residual unreacted sulfides (e.g., chalcopyrite and pyrite), the so-called S–S flotation.

During the pressure-oxidation process, most of the silver is converted into argentojarosite [$AgFe_3(SO_4)_2(OH)_6$]. Therefore, during the S–S flotation, most of the gold reports to the concentrate, while silver remains in the tailings. The S–S concentrate can be further processed, if warranted, by a sulfur-melting step, leaving behind residual sulfides and gold.

Direct cyanidation of the S–S flotation tailings could recover up to 90% of the gold but only 20% of the silver (locked as argentojarosite), with high consumption of cyanide (due to CNS formation) and lime (Berezowsky *et al.*, 1990). A typical S–S flotation tail assays 1.4 g/t Au, 220 g/t Ag, 45.6% Fe, 4.5% $S_{sulfate}$ and 3.3% S°. Attempts to further upgrade gold and silver from the flotation tailings by flotation or gravity separation were not successful. Leaching of the iron phase in acid/SO_2 resulted in a five-fold upgrading of the gold and silver but at prohibitive reagent costs.

Eventually, the silver enhancement treatment (SET) process was developed to destroy the jarosite by reaction with lime at 90°C (*hot boil*) and recovering the gold and silver from the hot-boiled product by standard cyanidation.

After sulfur melting and filtering, the S–S concentrate represents, in the case of the HBMS plant in Manitoba, only 6% of the weight of the original zinc concentrate feed, and it assays 1.8% Cu, 14.8% Fe, 24.7% Zn, 54.6% S_{total}, 33.5% S°, 12 g/t Au and 69 g/t Ag.

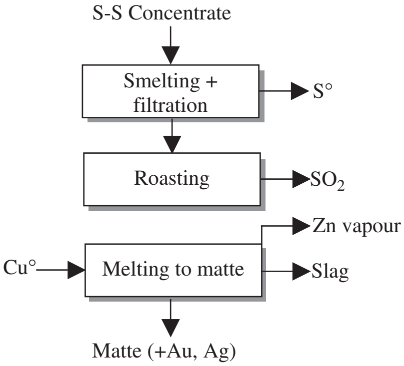

Fig. 16. Canmet proposed process to treat gold and silver residues from ZPL process.

A process developed by Canmet to recover gold and silver from that product is summarized in Fig. 16. (Skeaff, Craigen & Barlin, 1989).

Using this approach, 93–100% of the gold could be recovered in the matte.

As an alternative to matte smelting, several hydrometallurgical approaches were also evaluated, including thiourea leaching, acidic chlorination and cyanidation. Only cyanidation gave gold extractions high enough to be retained: gold extraction as high as 91.5% (silver extraction of 57%) but with a cyanide consumption of 48 kg/t.

4.3. Smelting of the zinc leach residue

In cases where zinc and lead smelters are fully integrated, such as at Cominco's Trail or Korea Zinc's Onsan Operations (De Groot and Verhelst, 2000; Kim Bae and Seung Lee, 2000), the option exists to treat the zinc leach residue in the lead smelter, as illustrated in Fig. 17 for Cominco.

Eventually, the gold and silver in both zinc and lead concentrates end up in the anodic slimes from the lead electrorefinery, and are recovered from there in the PMs refinery.

5. RECOVERY OF GOLD FROM LEAD CONCENTRATES

The association of silver with lead minerals, in particular galena [PbS], is well known and documented, but gold is also frequently found in lead concentrates, and its recovery follows closely that of silver.

5.1. Smelting processes

Galena concentrates are usually smelted to produce lead bullion. Smelting techniques are numerous, ranging from the traditional blast furnace to the more recent Kivcet, QSL and Ausmelt processes.

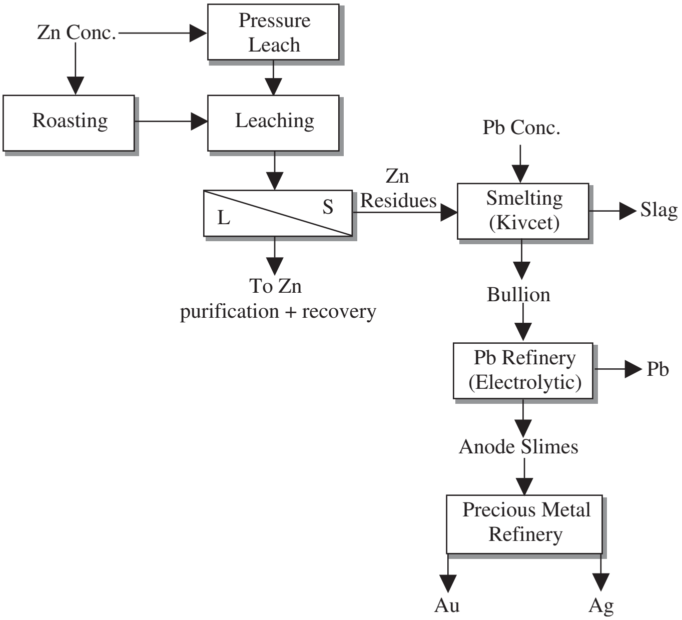

Fig. 17. Cominco's Trail integrated Zn, Pb operations (simplified).

The affinity of gold and silver for lead metal has been known since ancient times, and gold and silver are well collected in the metallic lead phase during smelting, irrespective of the type of melting process employed. Studies of PMs deportment in slags during smelting have confirmed the efficiency of the collection of PMs (gold + silver) by lead bullion (Matousek and Whellock, 1989). As an example, from a lead concentrate assaying 133 g/t Ag and 0.7 g/t Au, 99% and 97%, respectively, of the silver and gold are recovered in the lead bullion in Tsumeb (Mounsey and Piret, 2000).

The bullion is then processed to metallic lead using either thermal or electrometallurgical techniques (Siegmund, 2000), as illustrated in Fig. 18.

During the pyrometallurgical refining of lead bullion, silver and gold are removed to the target <10 g/t Ag typically using the Parkes process, whereby zinc metal is added to the lead bullion to form alloys with the PMs that are skimmed off during a batch or continuous process. The batch process as practiced by Pasminco's Port Pirie smelter in Australia (Kapoulitsas *et al.*, 2000) is illustrated in Fig. 19.

Typical lead bullions assay between 1,000 and 4,500 g/t Ag, with some exceptions like the Asarco St. Helena plant bullion (assaying 12–15,000 g/t Ag), the Met-Mex Penoles bullion (assaying ~15000 g/t Ag; Siegmund, 2000), and the Cerro de Pasco bullion (assaying up to 19,500 g/t (Au + Ag); Emicke *et al.*, 1970). Gold assays of the bullion are not usually reported but

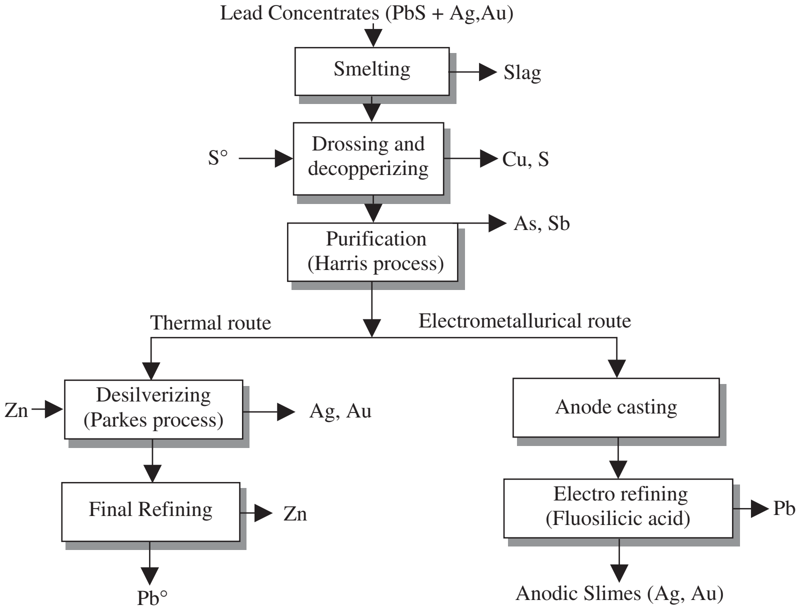

Fig. 18. Simplified processes for the recovery of gold and silver from galena concentrate after smelting.

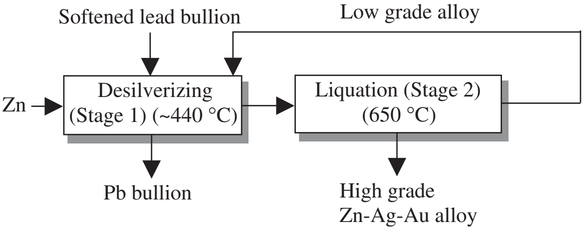

Fig. 19. Two-stage Parkes process at Port Pirie Smelter.

Cominco Trail operation reported in 2000 the production of 50,000 oz gold and 373 t of silver (Siegmund, 2000).

Depending on the operation, the PMs Zn alloy composition varies between 6 and 25% Ag. The alloy is then melted in a Doré furnace and the Doré silver is usually electrorefined in conventional Balbach Thum cells to produce 99.99% silver cathode, with the anodic slimes periodically collected and leached to produce a 98% gold product (Moor, 2000; Schupp, 2000).

During electrorefining, the composition of the lead anode slimes will vary depending on the starting lead anode composition; at Cerro de Pasco for

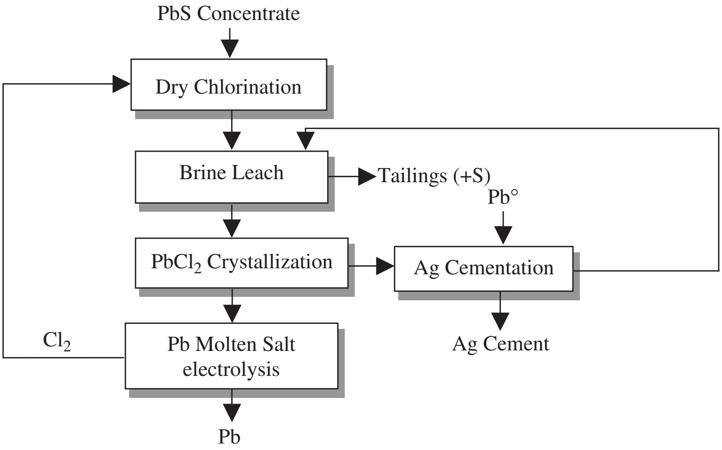

Fig. 20. Cymet process to recover lead and silver from galena concentrates.

example, anode slimes contained 35% Sb, 22% Bi, 14% Pb, 9% Ag and 1000 g/t Au (Aranda and Taylor, 1970).

5.2. Hydrometallurgy for lead concentrates

Various hydrometallurgical processes have been developed to produce lead from galena concentrates without going through a smelting stage. Cyprus Metallurgical Processes Corporation (Cymet) piloted a dry chlorination process that is illustrated in a simplified form in Fig. 20. (Reynolds *et al.*, 1977).

The results presented indicated extractions of 99% for both lead and silver. No mention of gold was made.

Ferric chloride leaching of galena has been investigated as early as in the 1920s. The main reactions involved are presented below:

$$PbS + 2FeCl_3 \rightarrow 2FeCl_2 + PbCl_2 + S^\circ \tag{4}$$

$$Ag_2S + 2FeCl_3 \rightarrow 2FeCl_2 + 2AgCl + S^\circ \tag{5}$$

The process is simply illustrated in Fig. 21.

This was the basis of the Minemet process (Demarthe and Georgeaux, 1980), which was piloted with good silver recoveries in Trappes, France at a 1 m^3 leach reactor scale. Solution purification consisted of cementation with

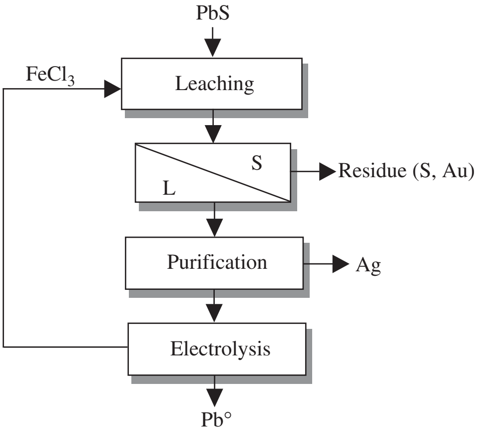

Fig. 21. Ferric chloride leaching of galena.

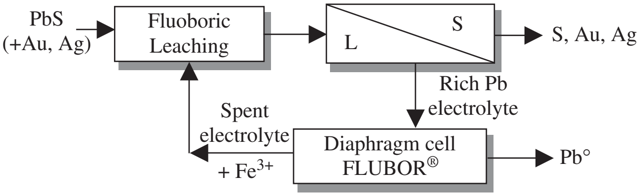

Fig. 22. Simplified flow diagram for the FLUBOR® process applied to lead sulfide concentrates.

lead powder for Cu, Ag and Bi, followed by final ion-exchange purification. Although gold was not mentioned in the reported results, it is unlikely that it was recovered since the oxidation potential of the ferrous/ferric couple is not high enough to oxidize gold under the typical leach conditions.

Variants of the ferric chloride leach for galena concentrates include the Canmet FCL process and the USBM process (Wong *et al.*, 1980). For the last cited process, lead recovery was effected by lead chloride crystallization and molten salt electrolysis of $PbCl_2$ crystals.

A recent process has been developed by Engitec that allows direct leaching of galena concentrate coupled with electrowinning of the lead directly from the leach solution (Olper *et al.*, 2000). A schematic diagram of the FLUBOR® process is presented in Fig. 22.

The chemistry underlying the FLUBOR® process is elegant, and can be summarized in the following reactions:

(a) Fluoboric leaching:

$$PbS + 2Fe(BF_4)_3 \rightarrow Pb(BF_4)_2 + 2Fe(BF_4)_2 + S^\circ \quad (6)$$

Galena is attacked by ferric fluoborate, to generate lead fluoborate, ferrous fluoborate and elemental sulfur. Gold and silver in the original galena feed are concentrated in the leach residue, which must be further treated to recover the PMs it contains.

(b) Electrolysis in the FLUBOR® Diaphragm cell:

Metallic lead is produced at the cathode, while the ferrous fluoborate is reoxidized to ferric fluoborate at the anode, as per the following half-reactions:

$$\textit{cathode}: \quad \mathrm{Pb(BF4)2} + 2\mathrm{e} \rightarrow \mathrm{Pb} + 2\mathrm{BF4}- \tag{7}$$

$$\textit{anode}: \quad 2\mathrm{Fe(BF_4)_2} + 2\mathrm{BF_4^-} \rightarrow 2\mathrm{Fe(BF_4)_3} + 2\mathrm{e} \tag{8}$$

This process has been piloted at a large scale at the Doe Run Company, Missouri, USA. No mention has been made of the recovery of silver and gold in that process.

6. RECOVERY OF GOLD FROM COBALT CONCENTRATES

Cobalt has traditionally been recovered as by-product of copper (in Central Africa) and nickel.

Gold is only rarely associated with cobalt minerals, but the occurrence exists. One such example is the NICO deposit in Canada where gold occurs associated with cobalt arsenides and cobaltiferous arsenopyrite. A process

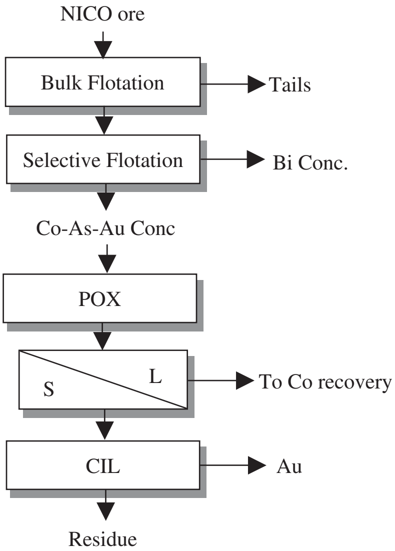

Fig. 23. Simplified process flowsheet for the NICO ore.

was developed to recover gold and cobalt from the NICO deposit, as indicated in Fig. 23 (Mezei *et al.*, 1999).

Using that process, 95% of the gold can be recovered using standard CIL on a pressure-oxidation residue. This process is currently being piloted for a pre-feasibility study.

7. RECOVERY OF GOLD FROM THE RECYCLING OF ELECTRONIC SCRAP

Electronic scrap is normally recycled to copper smelters, and therefore its PMs content is eventually recovered within the Cu refinery anodic slimes (Beke, 2001). There are plants, however, primarily dedicated to the treatment of electronic scrap. One such plant was the US Metals Refining (USMR) Company (Amax) plant in Carteret, New Jersey (Fruh, 1986; Manzone and Opie, 1977). About two-thirds of the 210,000 t/yr copper produced by USMR originated from scrap. The process can be described as illustrated in Fig. 24. The treatment of copper scrap consisted of copper smelting and converting, copper electrorefining, anode slimes purification by H_2SO_4 leach (to remove Cu + Ni), Doré smelting and silver electrorefining in a Thum cell, gold mud leaching with *aqua regia*, gold reduction with SO_2, and selective precipitation of red and yellow salts. When the amounts of PGMs (Ir, Ru, Rh) were such that they would become insoluble in the anodes, they were cast and treated batch-wise in a separate circuit: the silver was recycled to the main circuit, and the sludge was boiled in *aqua regia* to solubilize Au, Pt and Pd. The residue, containing Ir, Ru and Rh, was melted with Pb; the Pb–Rh alloy was leached with nitric acid to dissolve the Pb, and the crude rhodium purified. The (Ir + Ru)- rich nitric leach residue was fused with sodium peroxide to leach the Ru, while the residue was chlorinated and purified via the classical route to Ir powder (Hoffmann, 2002).

Further information on the recovery of gold from secondary sources, including spent autocatalysts and sweepings, may be found in Chapter 36.

8. DIRECT LEACHING OF GOLD AND PGMS FROM ORES OR CONCENTRATES

Present-day technology to treat high-grade PGM concentrates (smelting to matte, base metals refinery) is effective and well established. There are a few situations, however, where it is not suitable: (i) the concentrate is too low-grade or contains too many deleterious minerals for the smelter (*i.e.*, Cr_2O_3,

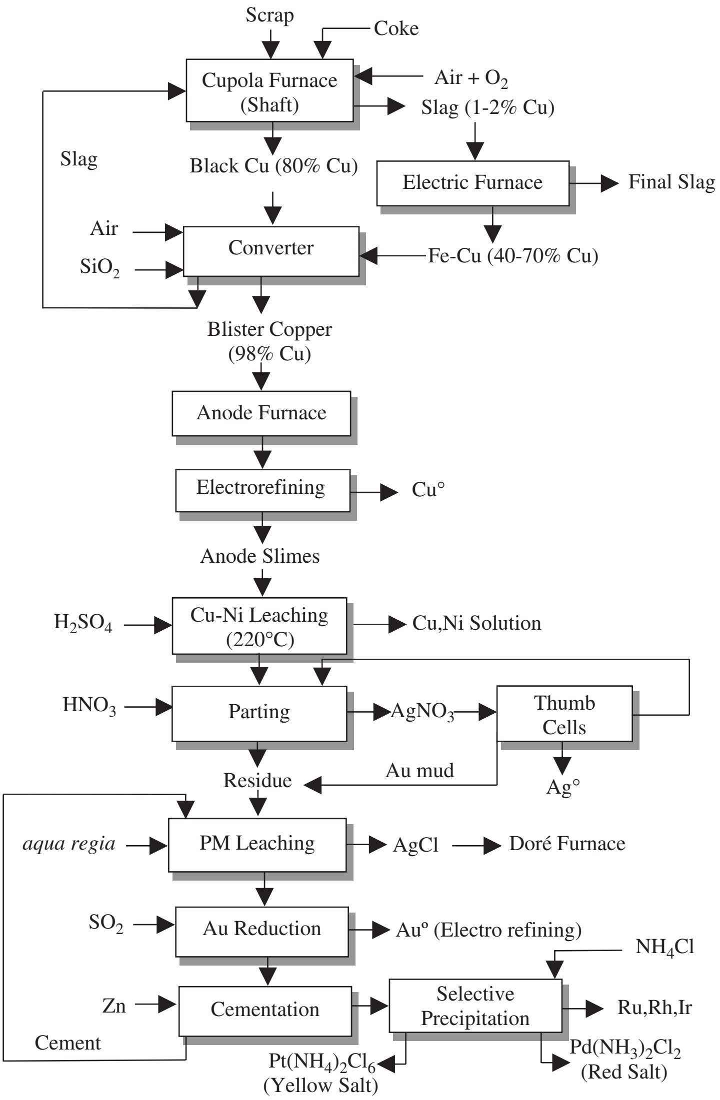

Fig. 24. Recovery of PMs from electronic scrap at USMR Carteret Plant.

MgO, As, *etc.*); (ii) the mine is remote and transportation costs to a centralized smelter would be prohibitive; and (iii) smelter contracts are not favourable to small operators.

Because of these potential issues, much effort has been devoted to the development of alternative process routes. Because hydrometallurgical plants are best suited for small operations, this is the direction usually taken by the organizations searching for alternative processes. A few of these emerging

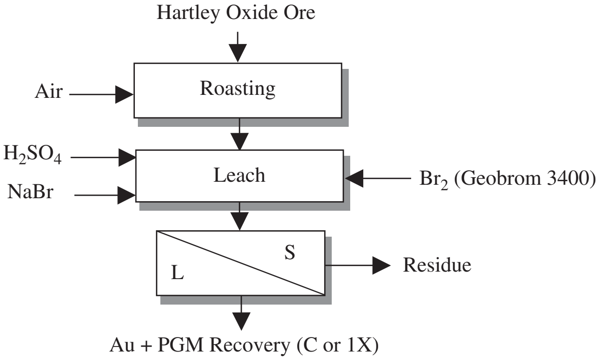

Fig. 25. Simplified TLM process diagram for the Hartley oxide ore.

new technologies will be described in the following pages; several other more recently developed processes may well have some potential, including the Panton process (roast/leach; Lewins and Greenaway, 2004) and the Liddell process (pressure oxidation/roast/leach; Liddell, 2003)

A discussion of the application of hydrometallurgical processes in PGM *refineries* can be found in Chapter 36, Section 3.

8.1. The BHP TML process

This process was developed to recover PMs (Gold + PGMs) from the oxidized portion of the Hartley deposit in Zimbabwe (Duyvesteyn *et al.*, 1994). A simplified flow chart diagram of the TML process is presented in Fig. 25.

The following were the recommended process parameters:

- Roasting: 300–700°C, 60–90 min, with air.
- Leaching: 70°C, 2 h, 100 g/L H_2SO_4.
- 10 g/L NaBr (>800 mV ORP with Br_2 using Geobrom 3400 as oxidant).
- 24–40% solids.

Geobrom 3400 is a sodium bromide solution in which liquid bromine is dissolved. It is a proprietary reagent manufactured by Great Lakes Chemical Company.

Under those conditions, recoveries were 90% Au, 85% Pt and 70% Rh.

8.2. The North American palladium process

This process was developed at Lakefield Research in the early 1990s (McDoulett and Reschke, 1994) for the treatment of the Lac des Isles PGM concentrate assaying 4–6 g/t Au, 4–6 g/t Pt, 50–80 g/t Pd, 2.5–3.0% Cu, 1.8–2.5% Ni, 12–12.5% Fe and 6–8% S. The patented process is illustrated in

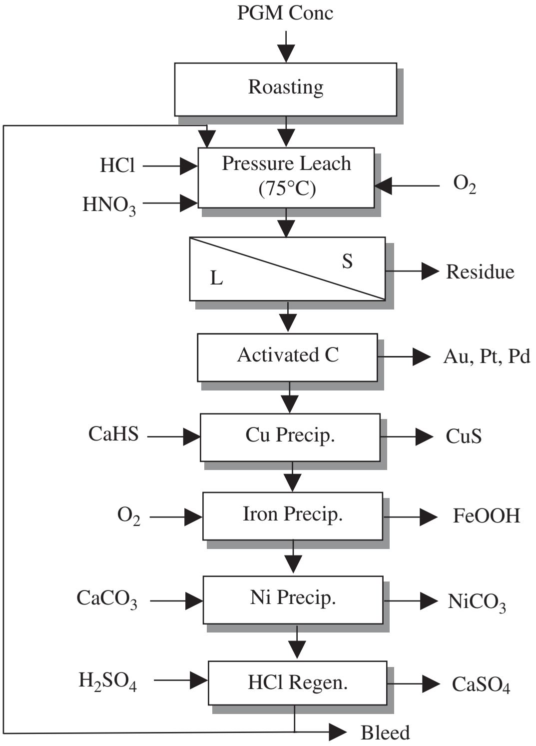

Fig. 26. Process flowsheet for the treatment of the Lac des Iles PGM concentrate.

Fig. 26. The process consisted of: partial oxidizing roast of the concentrate; pressure leaching (HCl/HNO_3) of calcine; filtration–washing, and activated carbon recovery of gold and PGMs. Under those conditions, recoveries were 95–98% Au, 94–95% Pt, 87–91% Pd, 78–96% Cu, and 82–92% Ni.

8.3. The PLATSOL™ process

The PLATSOL™ process was developed at Lakefield Research in the late 1990s by International PGM Technologies to treat PolyMet's NorthMet (formerly Dunka Road) deposit within the Duluth Gabbro in Minnesota, USA (Fleming *et al.*, 2000; Ferron *et al.*, 2000c, 2001). It is a high-temperature (>200°C) pressure-oxidation sulfate-based process with small additions of NaCl (5–20 g/L NaCl). Under those conditions, the base metals (Cu, Ni, Co) and the PMs (Au, Pt, Pd) are dissolved in one single step. The PGMs are then recovered from solution using NaSH, while Cu, Ni, and Co are recovered using conventional techniques. The proposed process flowsheet for the NorthMet concentrate is presented in Fig. 27. Results of a 10-day

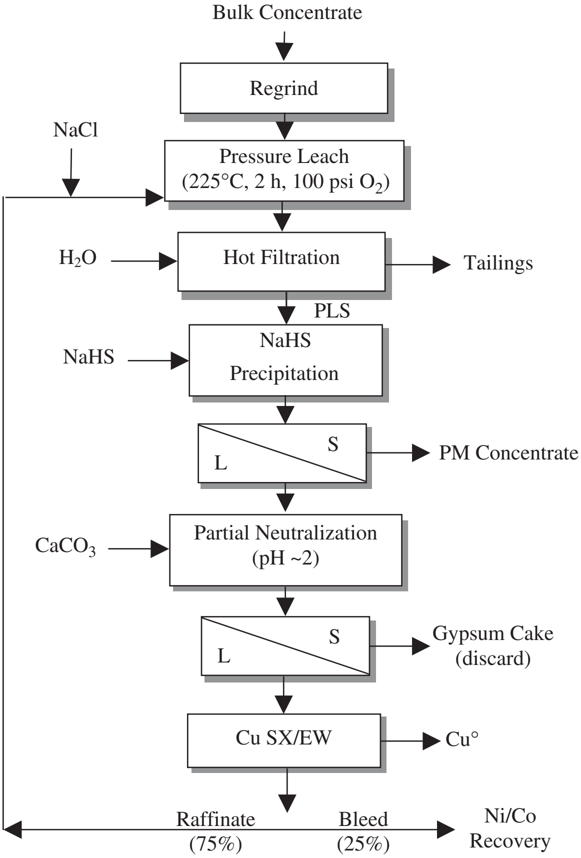

Fig. 27. Proposed process flowsheet to treat NorthMet bulk concentrate.

Table 2
Pilot plant results – PLATSOL™ treatment of the Northmet concentrate

	Feed	Steady state	
		Residue	Extraction (%)
Cu (%)	14.7	0.074	99.6
Ni (%)	3.05	0.047	98.9
Co (%)	0.14	0.006	96.0
Fe (%)	32.9	44.07	
Pd (g/t)	9.90	0.72	94.6
Pt (g/t)	2.22	0.12	96.0
Au (g/t)	1.41	0.20	89.4

integrated mini-pilot plant are summarized in Table 2. The process has also been applied successfully to numerous other PGM/Cu-Ni concentrates, as well as to Cu-Au concentrates, Cu–Ni–PGM mattes and Pt laterites (Ferron *et al.*, 2000a, 2000b; Fleming *et al.*, 2000; Ferron and Fleming, 2001).

Gold and the PMs in the leach solution can be recovered directly from the acidic liquor by sulfide precipitation, activated carbon or ion exchange (Ferron *et al.*, 2003).

9. CONCLUSIONS

As a by-product, gold is mostly recovered in copper smelters, and processes to recover gold from refinery anodic slimes are varied; just a few typical examples have been presented in this chapter. The fundamental reasons for the successful recovery of gold in the copper industry are, on one hand, the preferential association of gold with copper in sulfide ores (which makes for high gold content in copper concentrates), and on the other hand the natural concentration of gold in a very small mass (anodic slimes). This translates into a concentration factor of about 4 through the copper smelter, followed by a concentration factor of 100–200 in the electrorefinery. The result is a high gold-grade feed to the precious-metals plants. The same can be said for the gold in copper–nickel concentrates and PGM concentrates.

Gold in lead concentrates, although low in tenor, follows silver closely to the bullion into the Parkes concentrate or the anodic slimes, and is therefore well recovered.

The case of gold from zinc concentrates is different – gold tenor is typically fairly low in the concentrates; moreover, in existing processes, there is no stream wherein gold is well concentrated (except maybe the super-hot leach residue), and as expected, iron products (jarosites, basic iron sulfates and others) are the main contaminants. Notwithstanding, processes have been developed to recover gold from zinc concentrates, economics permitting.

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Chapter 36

Extraction of gold from platinum group metal (PGM) ores

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1. PRIMARY EXTRACTION CIRCUITS

The major portion of platinum and a significant portion of the palladium produced today originates from the Bushveld Igneous complex in South Africa. Beneficiation and recovery of platinum group metals (PGMs) from the major reefs involves a complex set of unit operations that has evolved greatly over the last few decades. Over time, a number of interesting flowsheets have been developed for the concentration, separation and purification of PGMs.

The major reefs mined today are the Merensky, UG2 and Platreef, with ore grades ranging from 3 to 8 g/t PGM and with associated nickel and copper in the 0.1–0.2% range present mainly as sulfides. Merensky reef has been the principal source of PGMs, and as demand for rhodium increased from the late 1970s exploitation of the UG2 now accounts for about half of the ore mined. Exploitation of the Platreef is a recent development; of the 10 producers only one currently mines Platreef on the northern limb of the complex.

World resources of PGM are estimated to total more than 100 million kg (Hilliard, 2004a, b). The annual production from the Bushveld Igneous complex is estimated in Table 1.

Gold from this source is estimated to be some 5 t/year and is considered to be a by-metal with the six PGMs, namely, platinum, palladium, rhodium, iridium, ruthenium and osmium.

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Table 1
Estimate of PGM production for 2003 from the Bushveld Igneous Complex (after Kendall, 2004)

	Pt	Pd	Rh	Ru	Ir	Total
Production (t/a)	150	70	16	9	4	250

Minerals in the Merensky reef associated with the PGMs are Pt–Fe alloys [Pt_3Fe], braggite [PtS], cooperite [(PtPdNi)S], moncheite [(PtPdNi)(TeBiSb)$_2$], kotulskite [(PtPdNi)(TeBiSb)$_2$] and laurite [(RuFeOsIrPt)S_2] (Vermaak and Hendriks, 1976; Corrans *et al*., 1982). Gold is present as electrum [Au_xAg_y] and associated with arsenian pyrite and arsenopyrite (Kinloch, 1982; Kinston and El-Dosuky, 1982; Chen *et al*., 2002).

The orebodies are milled and concentrated by froth flotation. Yields generally range from 60% for oxidized and high-chrome UG2 reef, to in excess of 90% for well-mineralized Merensky reef. The PGM content of this flotation concentrate varies between 100 and 1,000 g/t. Float concentrates are dried and smelted with burned lime as flux. Most furnaces in use are rectangular six-in-line slag-resistance furnaces operated with a submerged arc (Mostert and Roberts, 1973; Hodges *et al*., 1991). Temperatures of 1450°C or higher are required to form fluid slags allowing continuous tapping, whereas matte is tapped intermittently. Reflecting increasing volumes of UG2 processed, Lonmin recently commissioned a 12 m circular water-cooled furnace designed for high-power density to melt the higher chrome feeds.

Matte is composed of sulfides of Ni, Cu, Fe and PGM and at typical hearth operating temperature of 1200°C or higher the matte is very fluid. The distribution of gold between slag and typical Cu–Ni–Fe–S matte has been investigated (Celmer and Toguri, 1986; Choi and Cho, 1995). Distribution coefficients (K_d) of between 5 and 50 have been reported depending on the grade of matte. Tapped matte is transferred for further upgrading using Pierce–Smith converters. In this step iron and sulfur are removed by oxidation with oxygen-enriched air. Most of the iron is deported into a slag layer and the sulfur content is reduced to about 20%.

The primary producers have developed two processes for the subsequent treatments of the converter matte. Amplats use the slow-cooled converter matte process, where matte is cast into thermally insulated moulds to facilitate a slow rate of cooling, allowing the Ni–Cu sulfide phases to form distinct crystal habitats. Iron as an impurity is forced into the interstitial spaces between the Ni and Cu sulfide crystallites and concurrently concentrates the contained PGMs. The iron alloy produced this way is virtually free of metalloids such as arsenic, selenium and tellurium. Crushing and milling liberates the iron–PGM phase and is separated magnetically from the bulk of the matte. The efficiency of PGM deportment to the iron phase is as high as 97%. The iron alloy is leached to yield a final concentrate for input to the precious-metal refinery (PMR).

Impala and Lonmin practice a more traditional matte water-granulation process, as does Stillwater mining company (Montana, USA). This leads to a longer circuit to liberate the PGM contained and a poorer selectivity against metalloid elements. Granulated matte is first leached with sulfuric acid in a counter-current circuit for nickel extraction, followed by copper removal via a series of autoclaves using high temperature and high oxygen pressure. The finely divided leach residues are inputted to the PMR as final concentrates. The major disadvantage of this process concerns the metalloid elements that tend to concentrate with the PGMs, requiring further unit operations. Typical final concentrate feed assay to PMR is given in Table 2.

The three major producers have developed linear extraction circuits using crushing, flotation, smelting, converting and leaching to effect base metal/PGM separations. The typical process flow-circuits are detailed in Fig. 1.

2. GOLD EXTRACTION FROM SECONDARY SOURCES

The amount of gold that is recycled in the USA is substantial, and is in the range of 170–200 tpa (Amey, 1998). The main sources of scrap gold include discarded jewellery, scrap from jewellery manufacture, dental scrap, plating-bath solutions, scrapped electronic equipment, gold coins and medals. Additional sources include precipitates and sludges from base-metal refiners, anode slimes from copper refiners, gold-plating solutions, gold-bearing organo-metallic liquids and conductive inks and pastes.

Recycling precious metals is an extremely competitive business. The first priority is driven by the need to reach agreement with the customer on expectations of metal content, so preparation for sampling is an important part of the process. Shipments are accurately weighed and homogenized; this may include burning, shredding, melting and grinding to obtain a blend that

Table 2
Typical range of PGM in final concentrates after base-metal removal

	Au	Pt	Pd	Rh	Ru	Ir	Total PGM
Level (%)	0.9–1.8	36–40	17–22	4–5	7–11	1.4–2	60–80

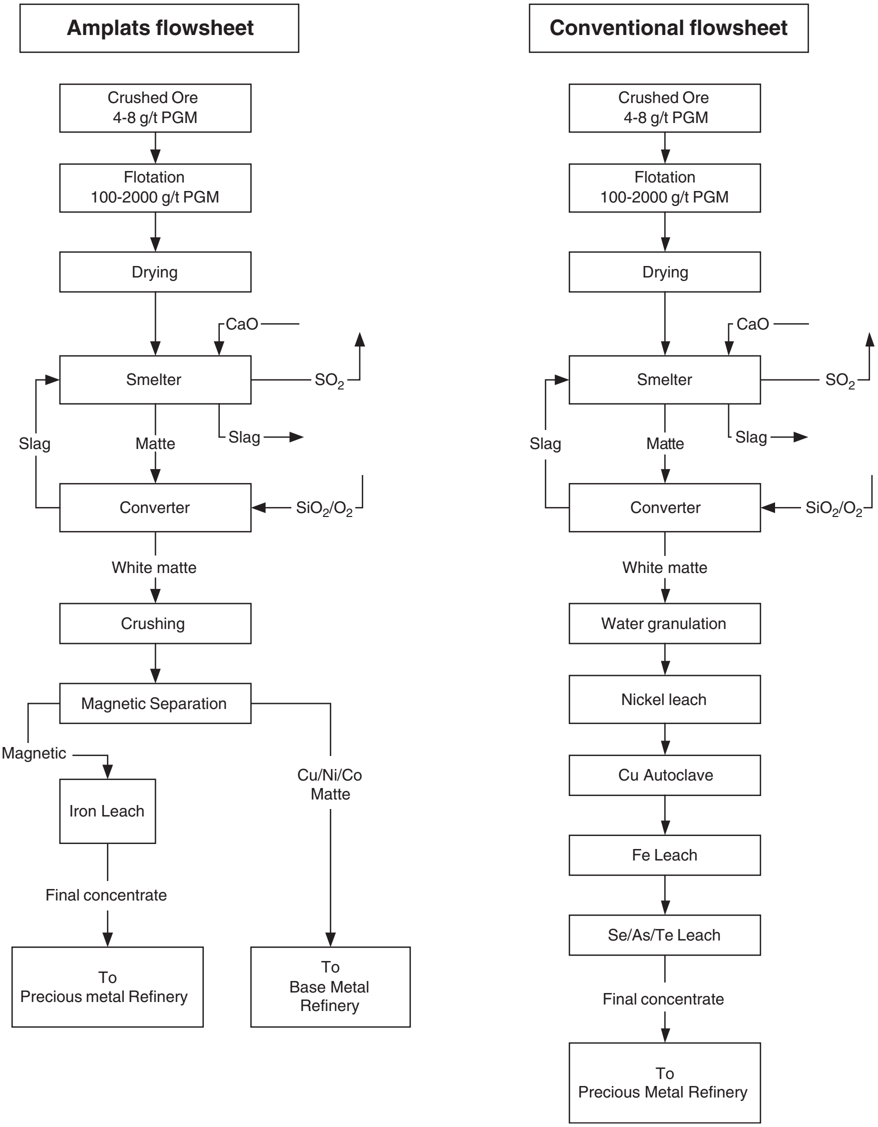

Fig. 1. Typical process circuits for the concentration of PGMs from sulfide ores.

can be accurately sampled. It is not uncommon for a client representative to be present at this step. Once representative samples are obtained, it is not unusual for the sample to be assayed by more than one accredited laboratory to determine the metal content for monetary settlement. Next is the output of metal in high yield and low cost in an environmentally sound and acceptable way.

2.1. Processing high-grade gold alloys

Refining alloys of greater than 30% gold content are well suited to the Miller process provided that the feed is free of PGMs. Alloys of this type are high-grade jewellery scrap, typically karat gold alloys and fillings. The impurities are in the main silver, nickel and copper. The Miller process is based on the fact that gold does not form stable chlorides above 400°C, whereas base metals and silver do.

The process involves melting the alloy and sparging chlorine gas into the melt with a quartz pipe. The first impurities to react are iron, zinc and lead, followed by copper and silver. The base metals and silver chlorides, being less dense, form a slag that can be skimmed off, and the end point is observed when a purple haze forms above the melt. The process is very effective in routinely producing gold purities in excess of 99.95%. This process is economical from the point of view that it is cheap to operate, is fast, and with experience very little gold deports to the slag, resulting in low metal inventory or lockup. Chapter 27 discusses the Miller process in more detail.

2.2. Refining gold–PGM alloys

Alloys containing gold, silver, PGMs and other metals are usually first processed using the Miller process to remove base metals and cast into anodes. Gold–PGM alloys are processed using the Wohlwill electrolytic refining process, also known as the gold cell. The Wohlwill cell uses impure gold alloy as anodes and deposits pure gold at the cathode. The electrolyte is made up as HCl and 100 g/L *tetra*chloroauric acid and is operate at 55–65°C. The cathode is made of titanium sheets to facilitate stripping off the plated gold, and the anodes are usually bagged to accumulate the anode slime. Gold produced from the gold cell is usually better than 99.97%. The composition of the anode slime is variable and usually contains a finely dispersed mixture of PGMs, silver and depending on the source, selenium, tellurium and lead.

The disadvantages of the gold cell method are the gold inventory required for the electrolyte, the long processing time to produce the anode slime and the subsequent time spent to refine the PGMs from the anode slime. A further disadvantage is the build-up of impurities in the electrolyte; this requires purging or complete change-out of electrolyte, with associated higher recovery costs.

2.3. Gold–copper alloys

Au–Cu alloys containing base metals can be processed in oxidized sulfate medium as shown by the generalized flowsheet in Fig. 2 (Subramanian *et al.*, 1980). Particle size is most important for effective dissolution, and is achieved by melting the alloy and water atomizing at pressures of 1000–5000 psig. A similar recovery circuit is used to process gold and

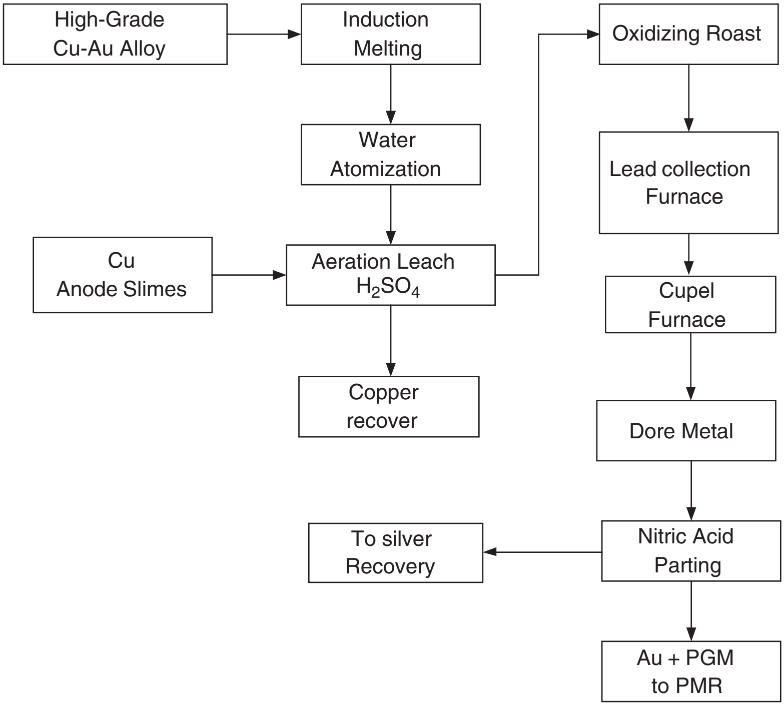

Fig. 2. Simplified separations circuit for recovery of gold and PGM from high-grade Cu–Au alloy and anode slimes.

precious metals from anode slimes, typically from copper electrorefining. Depending on the origin of the materials, anode slimes often contain selenium and tellurium, which require removal. Several process routes are used, either soda ash roasting (fritting) or NaOH fusion with a suitable oxidant, followed by water leaching.

Anode slimes high in copper can be roasted followed by sulfuric acid leaching for copper removal.

2.4. Low-grade Cu–Au–PGM

A further established process is the recovery of gold and PGM from electronic scrap. These materials are usually derived from shredding and grinding electronic components and boards followed by incineration. The ash is induction-melted and de-slaged and cast into anodes. These types of alloys are extremely variable in composition; they are largely composed of copper and small amounts of gold, silver, palladium, platinum and sometimes ruthenium. The balance is composed of the less desirable metals like lead, tin, bismuth, iron and aluminum. The anodes are processed electrolytically using sulfuric acid as the electrolyte. Copper is recovered at the cathode and the insoluble gold and PGM are recovered as anode slime.

Low surface area alloys such as grains are usually processed using aqua regia to achieve dissolution. The method of dissolution is very effective and is prevalent in the industry despite the cost disadvantage of specialized nitrous oxide scrubbing. Solutions generated are first de-nitrated by repeatedly boiling down with hydrochloric acid additions, followed by feeding into PMR separation circuits. The introduction of copper into PGM circuits is problematic, and additional steps are required to remove it without PGM losses.

2.5. Low-grade sweeps

2.5.1. Traditional methods

Lower-grade sweeps contain just about any combination of metals, metal oxides and salts. Typically, materials of less than 2–5% PGM are considered too low for hydrometallurgical leaching due to poor dissolution efficiency and high cost. Materials of this type are concentrated and separated from base metals via various smelting routes. Alloys produced are processed to further remove base metals, and final concentrates are dissolved and processed via hydrometallurgical circuits to recover gold and precious metals.

Perhaps lead collection is the most well-known smelting process (see also Chapter 27). A feature of this process is the relatively low temperature that is required to perform this pyrometallurgical unit operation. A limited variety of feeds can be processed via this method due to the requirement of a low-melting flux in the range 1,100–1,300°C and so excludes high-alumina feeds. Low-melting slags are formulated with suitable mixtures of lime, calcium carbonate, silicates, iron oxide, iron sulfide and borax. Fluid slags are a requirement for good metal recovery with the objective of forming discardable slag.

Lead oxide [litharge, PbO] is used with carbon as reducing agent to form the collector metal in the form of finely divided lead particles. As the particles collide and grow the influence of gravity causes the particles to drop through the molten slag and efficiently scavenge gold, silver and PGMs. The efficiency of the collection is promoted by using an excess of lead. Silver is inevitably present, and is often added to facilitate the melting and collection process by lowering the eutectic of the alloy formed. Smelting temperatures are in the range 1,100–1,300°C and lead, silver and gold remain molten since their melting points are 327°C, 962°C and 1064°C, respectively.

The formation of intermetallic compounds such as $AuPb_2$ enhances metal solubility in lead (Kubaschewski *et al.*, 1967). Similarly, platinum and palladium have melting points of 1,768°C and 1,555°C, respectively, and it is thought that intermetallic compounds such as PtPb and Pt_3Pb (with melting points of 795°C and 915°C, respectively) are part of the alloying with lead (Doerinckel, 1908).

Lead smelting is a versatile process; in the simplest form it is used for the assaying of gold bullion. The process can be modified to process complex feeds by adjusting the slag chemistry; iron can be removed by adding silica to form an iron–silicate slag phase such as fayalite [Fe_2SiO_4]. Copper and nickel can be removed by the addition of sulfide to form a matte phase between the slag and the molten lead phase.

A number of process routes have been developed to recover the gold, silver and PGMs from the lead phase. Cupel furnaces and more recently top-blown rotary converters, have been used to oxidize the lead into lead oxide (PbO). The volatile lead oxide is recovered for recycling by cooling the fume and filtering the stream though high-efficiency bag-house filters. The alloy, now deficient in lead, is called *Doré*. The alloy is grained and leached with nitric acid to dissolve silver and base metals. The residue is composed of insoluble gold and PGMs as a finely divided sponge. The sponge is processed via conventional hydrometallurgical circuits.

Lead alloys can also be treated using the Parkes process to recover the gold, silver and precious metals (Karsten, 1829, 1834; Parkes, 1850, 1852). In this process the molten lead alloy is covered with a layer of borax and zinc metal is stirred into the batch with vigorous mixing. A zinc crust is formed that dissolves gold, silver and precious metals and floats to the top of the melt. This zinc treatment is repeated to dross all the precious metals. The dross crust is skimmed off and the processed further to recover the valuable metals (Kirchholt, 1878).

The long-term use of lead as a process option is limited by the health and safety concerns of handling lead and lead oxide fumes, and it is doubtful if any new plants would be built in the USA or elsewhere in the world.

2.5.2. Modern low-grade circuits

The availability of large volumes of catalytic converters from automobiles (*autocats*) has lead to the development of smelting technologies based on iron and copper collection (Mishra and Reddy, 1987; Hoffmann, 1988). Engelhard has developed pyrometallurgical and hydrometallurgical technologies to concentrate and refine a variety of materials containing low grades of precious metals, including gold (Benson *et al.*, 2000). This is a departure from typical autocat smelters, where gold is not considered as an input to the furnace.

The smelter is a 2.5 MVA submerged carbon arc with a circular three-electrode (AC) and is operated as a slag-resistance furnace. The power density of this specialized furnace is relatively high at 320 kW/m^2 to deal with the high-alumina feeds. The furnace is refractory lined and chilled with three water-cooled copper plates for the development of a freeze liner. The operation is semi-continuous; slag is tapped every 3 h though a water-cooled cinder monkey, while alloy is tapped once a day through a tapping hole in an alumina block. A mud gun is used to open and plug the alloy tap-hole, and the slag tap-hole is opened and closed by hand.

The off-gas stream is passed through a thermal oxidizer to oxidize CO to CO_2, and mixed with cooling air and filtered using a static bag-house for primary cleaning. The off-gas is then scrubbed with caustic, and passed though an electrostatic precipitator before final discharge to the atmosphere.

A rather large variety of materials are available for smelting, and includes refinery residues generated from internal hydrometallurgical refining circuits; autocatalysts from internal manufacturing and after market sources, and spent catalysts from the chemical industry. Refinery residues are insoluble materials, typically leach resides containing significant PGM content, including gold and silver together with significant amounts of sodium and chloride.

Autocat manufacture generates a considerable volume of waste materials with small but significant PGM contents. These ceramic substrates are high melting-point aluminosilicates, namely, cordierite [$Mg_2Al_4Si_5O_{18}$] and mullite [$Al_6Si_2O_{13}$], with varying amounts of alumina. The after-market autocats vary considerably in PGM content, with contaminants that include iron, nickel, chrome, lead, phosphorus, zinc and rare-earth metals like CeO_2.

Spent catalysts are refractory materials with a large spread of compositions ranging from alumina, aluminosilicates, zeolites, and silicates to silicon carbides. Metal content ranges from 0.1 to 5% PGM, and compositions range from single PGMs (Pt on Al_2O_3), and single PGM plus base metal (Pt/Fe on Al_2O_3), to mixed PGM (Au/Pd on Al_2O_3). These materials usually have relatively small PGM contents and high-surface areas and do not respond well to leaching owing to the considerable loss of PGM that takes place by re-adsorption.

The more traditional sweeps are also added to the smelting circuit and include jewellers sweeps that are typically less than 0.1% gold as well as polishing *rouge*, which are mixtures of refractory abrasive materials such as iron oxides, corundum [$Al_6Si_2O_{13}$] and alumina [Al_2O_3]. The smelting of such complex mixtures requires good chemical analysis for calculation of lime and other flux additions for the formation of fluid slags in the range 1500–1600°C. To achieve this reference is made to the ternary phase diagrams for $CaO–Al_2O_3–SiO_2$ and $CaO–FeO–SiO_2$ when compounding smelter blends.

The collection mechanism in essence utilizes the carbothermic reaction between hematite and carbon to form finely dispersed iron particles that act as the collector. Smelting conditions are considered to be oxidizing, where most of the iron is deported to the slag as FeO, but some of the iron oxide is

Table 3
Distribution coefficients for PGM under typical smelting conditions

Element	D_x
Au	130
Pt	600
Pd	1100
Rh	230

D_x (% (m/m) of metal X $)_{\text{alloy}}$/(% (m/m) of metal X$)_{\text{slag}}$.

reduced to metal, forming a dense finely dispersed metallic phase. The finely dispersed iron collector rains through the molten slag, colliding with gold and PGMs, and once a critical particle size is reached gravitational forces cause the particles to settle on the hearth.

The main carbothermic reactions are summarized as follows:

$$Fe_2O_3 + C \rightarrow 2FeO + CO\ (g) \tag{1}$$

$$FeO + C \rightarrow Fe + CO\ (g) \tag{2}$$

Iron oxide is not the only source of collector metal. At temperatures of 1,600°C most metal oxides are reduced to metal, resulting in additional metal fall that dilutes the PGM content of the alloy. This is especially true in the presence of SiO_2, where reduction to silicon is thermodynamically favourable at temperatures greater than 1,600°C. The reduction results in the formation of ferrosilicon in the alloy, which is undesirable from a hydrometallurgical point of view. The alloy formed has a density of 7–8 g/cm^3 and is significantly denser than the slag that is typically 2–4 g/cm^3. The PGM content of the alloy produced is usually in the range 10–15%.

The distribution coefficients D_x of metals of interest between alloy and slag phase are summarized in Table 3.

Fig. 3 shows a typical flowsheet for the concentration of PGMs from alumina and aluminosilicate feeds via smelting and hydrometallurgical unit operations.

3. HYDROMETALLURGICAL GOLD PROCESSES IN PRECIOUS METAL REFINERIES

Hydrometallurgical techniques have the potential of low-capital costs and automation. Most recently, extensive use of solvent extraction and resin technologies has been successfully applied for the selective extraction and concentration of PGMs.

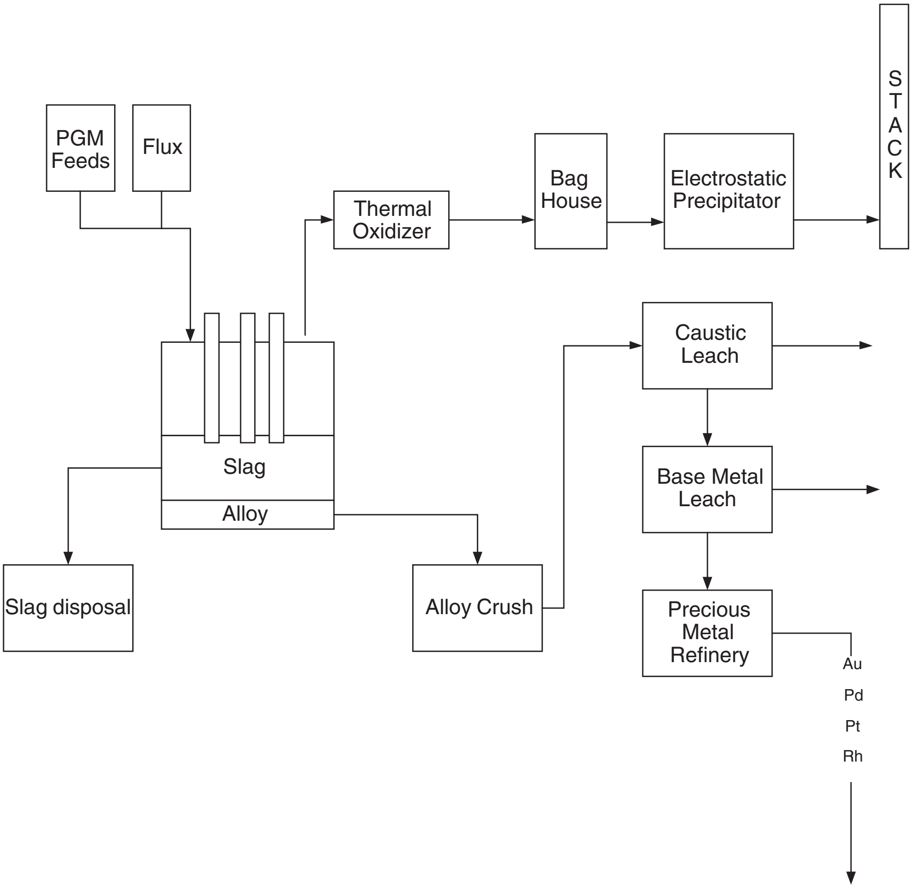

Fig. 3. Typical flowsheet for smelting and leaching catalytic converters.

PGM refineries input concentrates and alloys that are inevitably mixtures of PGMs, and base metals with gold and silver as minor constituents of the complex mix. The presence of other metals such as selenium, tellurium and arsenic often detract from the use of solvent extraction due to the co-extraction and formation of interface cruds. Hence great efforts are taken to remove these deleterious elements early in the process. Fig. 4 outlines a number of modern separation circuits. Details are highly confidential, although some details have been published (Grant, 1980; Renner, 1992).

3.1. Dissolution of concentrates and alloys

Atmospheric dissolution and pressure dissolution with hydrochloric acid–chlorine is usually the method of choice. The dissolution process is greatly facilitated by the extremely fine leach residues obtained from high-pressure autoclave leaching of matte and Doré leach residues containing

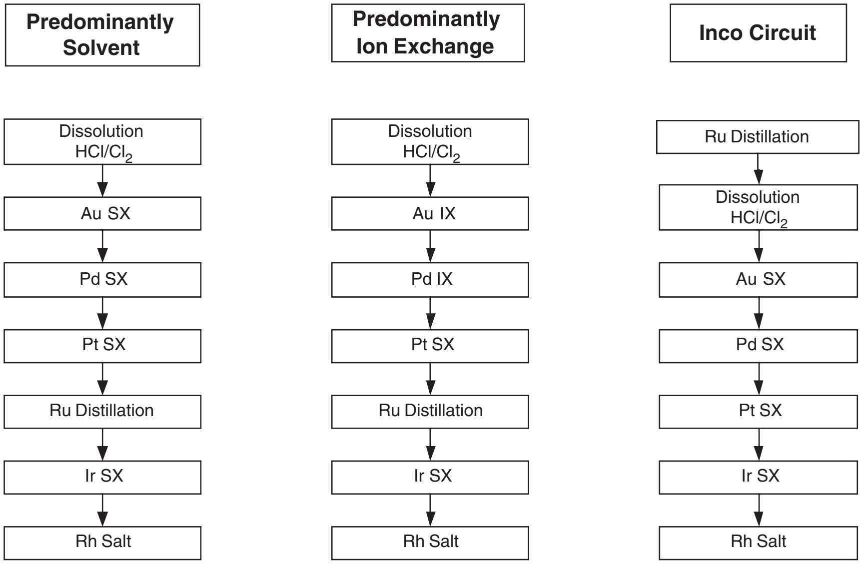

Fig. 4. Modern precious-metal separation circuits.

PGMs. Bulk alloys can be atomized to increase surface areas, facilitating the dissolution process. *Aqua regia* is effective for rendering granulated alloys into solution. Although it is an effective dissolution technique, multiple boil-down steps are required to de-nitrate the solutions. Boiling down the solutions to expel hydrochloric acid, followed by water dilution isolates silver chloride. Adjustment of solution potential is required to ensure the correct oxidation state of metal chloride species for subsequent separation steps.

3.2. Selective gold extraction and recovery from complex PGM solutions

Once in solution as the *tetra*chloroauric complex a number of commercial processes are used to isolate gold from PGMs and base metals. Reduction of gold to the metal is used for batch processes, and solvent extraction is often used for continuous processes. Resin technology has been used for large-scale gold adsorption, and more recently a number of solvent-impregnated resins have been investigated (Villaescusa *et al.*, 1990, 1992).

3.3. Selective reduction of gold in PGM solutions

The classic process involving reduction of gold to metal from chloride solution is a simple and effective process that is well suited to batch operation. A large number of reagents have been used, namely hydrazine, SO_2 gas, oxalic acid, *bi*sulfite, sucrose and others. Overall, most reagents provide fairly selective gold reduction in the presence of large excesses of chloro-complexes such as Pt, Pd, Rh, Ir, Ru and base metals. Pure gold is seldom obtained on the first precipitation; the main objective is to remove all the gold from the high-value stream.

Hydrazine as the hydrochloride is an effective reducing agent for gold in the presence of significant concentrations of metalloids such as selenium and tellurium. Hydrazine is slowly added to the boiling solution and the solution potential is taken to 400 mV (saturated calomel electrode, SCE), and the solution is boiled to coagulate the gold particles.

The reaction is given by

$$HAuCl_4 + \tfrac{3}{4}N_2H_4 \rightarrow Au(\downarrow) + 4HCl + \tfrac{3}{4}N_2 \qquad (3)$$

The main reaction product is nitrogen gas. However, side reactions take place and result in the formation of ammonium ions. This leads to the contamination of the gold by the precipitation of ammonium salts of platinum and palladium. A further problem is the co-precipitation of selenium and tellurium, depending on the solution conditions.

A useful method for the reduction of gold chloride to metal makes use of SO_2 gas. This method is selective, and a pure gold precipitate is produced when the process is split into two parts. An early cut-off where 90% of the gold is precipitated ensures that good quality gold is obtained. The second part can be more aggressive and almost all the gold can be removed from solution. The reaction is shown below:

$$2HAuCl_4 + 3SO_2 + 6H_2O \rightarrow 2Au(\downarrow) + 3H_2SO_4 + 8HCl \qquad (4)$$

The use of SO_2 gas leads to the formation of complexes with palladium such as sulfoxides and sulfates, which impact the separation of palladium from downstream unit operations. Further, the presence of sulfate in the solutions results in precipitation of lead and silver, which often contaminate the gold precipitate.

Perhaps oxalic acid is the most selective reducing agent for the reduction of *tetra*chloroauric acid from solution. Oxalate is a mild but sufficiently strong reducing agent for the reduction of gold in the presence of large amounts of PGMs in solution.

The reaction is given by

$$2HAuCl_4 + 3C_2H_2O_4 \rightarrow 2Au(\downarrow) + 8HCl + 6CO_2 \qquad (5)$$

The reduction of the *tetra*chloroauric acid from solution using the Fe(II)/Fe(III) couple is an especially selective process against PGM. The slow addition of a concentrated solution of Fe(II) sulfate to a warm solution precipitates a fine gold powder that is usually better than 99.95% gold sponge.

The reaction is given by

$$\mathrm{AuCl_4^- + 3Fe^{2+} \rightarrow Au(\downarrow) + 3Fe^{3+} + 4Cl^-} \tag{6}$$

As mentioned, acceptable gold purity is obtained with difficulty on the first pass using reductive methods. Depending on the impurities present, the impure gold is routinely reworked, often a number of times, to achieve purity.

The Miller process can be used when PGMs are minor contaminants. Either the oxalate reduction process, or the ferrous salts reduction process, can be used after re-dissolution of the gold.

3.4. Selective solvent extraction of gold from PGM solutions

Several commercial processes exist for the selective extraction of chlorocomplexes of PGMs and gold from aqueous solution (Rimmer, 1974; Cleare *et al.*, 1981).

Amines have been extensively investigated as ion-exchange reagents, both in solvent exchange and in stationary-phase applications. In general, the strength of the interaction of amines with anions is given by the following sequence:

$$\text{quaternary ammonium salt} > \text{tertiary amine} > \text{secondary amine} > \text{primary amine}$$

The ion exchange process is summarized in the reaction shown below (Eq. (7)). The first step is protonation of the amine (where $n = 1$–4 long-chain aliphatic or branched-chain aliphatic groups), followed by exchange of the chloride anion by the *tetra*chloroaurate anion:

$$[\mathrm{R}_n\mathrm{N}]_{\mathrm{org}} + \mathrm{HCl}_{\mathrm{aq}} \rightarrow [\mathrm{R}_n\mathrm{NH^+Cl^-}]_{\mathrm{org}} \tag{7}$$

$$[\mathrm{R}_n\mathrm{NH^+Cl^-}]_{\mathrm{org}} + \mathrm{AuCl}^-_{4\mathrm{aq}} \rightarrow [\mathrm{R}_n\mathrm{NH^+AuCl_4^-}]_{\mathrm{org}} + \mathrm{Cl}^-_{\mathrm{aq}} \tag{8}$$

The problem with amine solvents is with the strength of the ion pair formed. Solvents based on quaternary-ammonium salts form very strong ion pairs, and once formed are essentially irreversible. The extraction of *tetra*chloroauric anion with *octa*decyl*di*methylbenzylammonium chloride results in an extremely strong interaction with a reported distribution coefficient $K_{\mathrm{d}} \sim 3 \times 10^5$ (Jin-Xin *et al.*, 2003).

Strong bases have not found much commercial application in PGM circuits other than as metal scavengers from dilute streams. Readily available commercial quaternary ammonium ion-exchange resins are used to recover small amounts of PGMs and gold from dilute solution. In practice, adsorbed metal is recovered by burning the resin.

Ternary, secondary and primary amines have found commercial application in PGM extraction circuits (Grant, 1980). Distribution coefficients (K_{d})

Table 4
Distribution coefficients for extraction of PGMs and gold from 6 M HCl by *tri*octylamine

Complex	K_d
$AuCl_4^-$	10^5
$PtCl_6^{2-}$	800
$PdCl_4^{2-}$	10
$RhCl_6^{3-}$	0.01

for extraction of the chloro-complexes of PGMs and gold by *tri*octylamine are shown in Table 4. However, the extraction coefficient for gold chloride is very large, and interacts too strongly with the anion, so that stripping is difficult to achieve (Alguacil and Caravaca, 1993; Alguacil *et al.*, 2001).

Solvent-extraction circuits for primary producers of PGMs are complex due to the multi-component metal ions present, as illustrated by the flow of material shown in Fig. 3 above. After gold recovery, the next metal to be solvent extracted is palladium. This is achieved using ligand-replacement complexation with either an oxime (*e.g.*, LIX 85N) or *di*octyl or *di*hexyl sulfide. This is followed by the extraction of platinum with a ternary or secondary amine.

Secondary producers usually have less complex mixtures that include platinum, palladium, rhodium and minor amounts of base metals. Separation circuits typically include co-extraction of the anions $PtCl_6^{2-}$ and $PdCl_4^{2-}$ in low-acid conditions using solvents such as *tri-iso*octyl amine (*e.g.*, Alamine 336 or 308) or using branched-chain sterically hindered tertiary amines (*e.g.*, Primene JMT). Once separated, the metals are back-extracted into strong hydrochloric acid, essentially reversing the ion exchange over a number of stages using strong chloride. Further processing of the separated metals includes the classic yellow and red salt processes. Similarly, the rhodium stream, now free of palladium and platinum, is processed via classical methods.

Selective solvent extraction of the *tetra*chloroauric anion is achieved when less basic groups than amines are used to form the ion pair. Solvents based on oxygenated organic groups such as polyethers, ketones and alcohols are weakly basic, and these moieties interact weakly with the *tetra*chloroauric acid. Further, no appreciable interaction of the weak oxygen-base groups with anions with double and triple negative charges takes place, according to the series below, reflecting charge on the anion and the charge-to-size ratio:

$$AuCl_4^- \gg PtCl_6^{2-} > PdCl_4^{2-} \gg RhCl_6^{3-}$$

The mechanism of extraction first involves the formation of a protonated ion pair between the organic and hydrochloric acid, followed by ion exchange of the *tetra*chloroauric anion for chloride, as shown in the reactions below (Eq. (9) and (10)) (waters of hydration ($n = 1$–4) are omitted for the purpose of clarity):

$$[R_2O]_{org} + HCl_{aq} \rightarrow [R_2O(H_3O)^+Cl^-]_{org} \tag{9}$$

$$AuCl^-_{4aq} + [R_2O(H_3O)^+Cl^-]_{org} \rightarrow [R_2O(H_3O)^+AuCl_4^-]_{org} + Cl^-_{aq} \tag{10}$$

The mechanism of the extraction process has been investigated in detail (Sargent and Rice, 1977). The process is thought to involve solvated ion-exchange, where the oxygenated functional group weakly interacts with a hydrated proton, and the *tetra*chloroauric anion is exchanged for chloride with no direct interaction with the polarizable Au(III) moiety. The selectivity for gold is attributed to the low charge-to-size ratio of the $AuCl_4^-$ (Sargent and Rice, 1977; Fieberg and Edwards, 1978). Evidence, principally based on UV/visible, infrared, far-infrared and Raman spectra, showed that the square-planar $AuCl_4^-$ anion in the organic phase was essentially identical to that present in aqueous medium.

3.5. Gold solvent extraction with dibutyl carbitol

Dibutyl carbitol, or more correctly, *diethylene glycol dibutyl ether* (also known as *butex* and *butyl diglyme*) was the first gold-selective solvent-extraction system to be commercialized by Inco at the Acton Refinery (Morris and Khan, 1968; Barns and Edwards, 1982). Advantages of this solvent are high selectivity for gold, low volatility (boiling point, 254°C), high flash point (118°C), and relatively low solubility in water (0.3%).

The extraction of *tetra*chloroaurate anion in acid medium with dibutyl carbitol is extremely fast and can be performed using batch extraction or mixer-settlers. The distribution coefficient for gold extraction into the organic phase is large, and is of the order of $K_d \sim 2500$. Extraction of *tetra*-chloroauric acid is independent of hydrochloric acid concentration, and solvents can be loaded to more than 100 g/L gold without phase inversion.

Fig. 5 represents a model of the ion-pair formed between the extracted *tetra*chloroauric anion, and the protonated dibutyl carbitol solvent. The proton most probably has multiple waters of hydration.

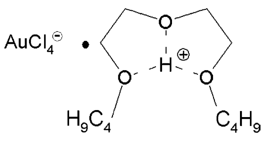

Fig. 5. The protonated dibutyl carbitol and *tetra*chloroauric ion-pair.

The selectivity of dibutyl carbitol against PGMs and most base metals is very good, the exceptions being iron, and to a lesser extent, platinum. Iron, in the form of the tetrahedral *tetra*chloroferrate anion $FeCl_4^-$, competes for extraction, but requires a large excess of protons to force the equilibrium to the right. The small amount of platinum extracted is attributed to a favourable charge-to-size ratio formed between the large neutral protonated *hexa*chloroplatinate anion and the oxygen groups.

The thermodynamics of extraction of $AuCl_4^-$ anion with *di*butyl carbitol in 1.5 M HCl have been investigated, and were found to be exothermic (Hol *et al.*, 1982): $\Delta G^\circ = -8.51$ kJ/mol, $\Delta H^\circ = -84.24$ kJ/mol and $\Delta S^\circ = -0.25$ kJ/mol K.

Impurities are managed with dilute acid back-stripping of the loaded solvent. The process requires multiple contacts, leading to small but significant gold and solvent losses.

Stripping is achieved using oxalic acid and heating to 50°C, to produce a granular gold powder that is isolated by filtration. The gold requires calcination to remove the organic. Gold that is produced is routinely 99.99% (Demopoulos, 1992).

The reduction is given by Eq. (11) (waters of hydration are omitted):

$$2[R_2O(H_3O)^+AuCl_4^-]_{org} + 3H_2C_2O_4 \rightarrow 2Au + 6CO_2 + 8HCl + 2[R_2O]_{org} + 2H_2O \tag{11}$$

The main drawback of this process is the water solubility of the organic, leading to solvent losses to the acid raffinate, scrub liquors and stripping stage.

3.6. Gold solvent extraction with MIBK

A more recent commercial example of gold solvent extraction is MIBK (methyl *iso*butyl ketone), which is used by Amplats at the SAREF facility (Nachtrieb and Conway, 1950; Claere *et al.*, 1979). Mixer-settlers are used with nitrogen blankets due to the flammable and volatile nature (flash point, 17°C, boiling point, 114°C) of the organic ketone.

Extraction kinetics are fast and virtually instantaneous. The distribution coefficient for *tetra*chloroaurate is reasonably high at $K_d \sim 1{,}000$, and is independent of acid concentration in the range 1–6 M HCl. In practice, solvent loadings of 15–20 g/l are targeted to polish the PGM stream of gold. The acid concentration greatly influences MIBK selectivity for gold, and significant co-extraction of Fe(III), Te(IV) and Pt(IV) takes place even when the extraction is conducted in 1.5 M HCl. Solvent scrubbing is required to back-extract impurities.

Stripping is conducted with reducing agents such as oxalic acid, with gentle heating. Gold particles are recovered by filtration and purity after calcination is usually 99.95%. MIBK is relatively insoluble in water and mild acid, and only 0.3% of the solvent is lost per cycle.

3.7. Gold solvent extraction with 2-ethyl hexanol

Selective solvent extraction of *tetra*chloroauric acid from complex PGM solutions using 2-ethyl hexanol (2-ethyl-1-hexanol) offers distinct advantages over the solvents described above. This branched-chain alcohol has the reasonably high flash point of 73°C, and a boiling point of 179°C. The alcohol is relatively inexpensive, freely available, practically odorless, and most importantly reasonably insoluble in water (0.05%) and dilute acid (0.1%). The distribution coefficient for *tetra*chloroaurate is reasonably high at $K_d \sim 1500$, and is independent of acid concentration in the range 1–6 M HCl. Gold extraction is fast and selective, although significant co-extraction of Fe(III), Te(IV) and Pt(IV) takes place even when the extraction is conducted in 1 M HCl. Impurities can be scrubbed with 1 M HCl without undue solvent loss.

Stripping can be achieved using the oxalic acid reduction method to yield gold sponge that requires calcination to remove adsorbed solvent. Sponge purity is in the 99.99% range. Stripping the solvent of gold is also possible using a dilute carbonate solution to neutralize the proton, causing abstraction of the *tetra*chloroauric anion into the aqueous phase. This process (see Eq. (12)) is extremely fast, and has the advantage of keeping the gold in solution, thereby allowing further process options:

$$[R_2O(H_3O)^+AuCl_4^-]_{org} + NaHCO_3 \rightarrow AuCl_4^- + CO_2 + 2H_2O + Na^+ + [R_2O]_{org} \quad (12)$$

The *tetra*chloroauric anion is relatively stable towards hydrolysis, provided that the strip solution is re-acidified with hydrochloric acid without too much delay.

3.8. Ion exchange

Selective adsorption of *tetra*chloroaurate anion in acid solution by the resin Amberlite XAD-7 has been investigated (Edwards *et al.*, 1976; El Ci *et al.*, 1994). The polymeric adsorbent has a rather large surface area of 500 m^2/g, and is composed of a polyacrylate matrix with aliphatic ester groups ($R\text{-}CO_2$). The resin is selective for gold in typical PGM streams, and when operated as typical ion-exchange columns, the resin has a gold capacity of 10–15 g/L. Co-extraction of Fe(III) and Pt(IV) takes place, but these metals can be displaced with water and dilute acid column scrubs.

Stripping is conducted with a weak base to yield a solution of *tetra*chloroauric that is stabilized with hydrochloric acid. Purity is not readily achieved in practice. However, the technique is useful in the separation and polishing of gold from PGM streams. Further, the process of adsorption, washing and elution is relatively simple to automate, and can be operated in a semi-batch manner.

4. CONCLUSIONS

The igneous techniques developed for the recovery of gold from primary and secondary sources mirror the state of the art in the field of extractive metallurgy. In some respects extraction techniques have in essence not changed for centuries, an example being fire assay practice. On the other hand, more advanced extractive techniques have only recently been developed, an example being selective solvent-extraction.

Undoubtedly, economic considerations will continue to drive the ongoing discovery and development of metallurgical techniques and processes to perform cheaper, faster and hopefully drive the industry towards more sound environmental practices.

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George Kyriakakis graduated at the University of the Witwatersrand with an MSc in 1992. He joined Engelhard in 1997 as Technology Manager to develop precious-metal refining technologies and specialized precious-metal salts and solutions for chemical and automobile catalyst manufacture. He successfully established smelting and hydrometallurgical technology for Engelhard Corporation to compete globally for the recovery of PGMs from high-alumina feeds, refinery residues and autocatalysts. George was previously employed by Western Platinum in South Africa, positions including R&D, Projects and Refinery Manager. He was instrumental in the development of the linear separations process for the seven precious metals, including a novel rhodium and iridium purification process resulting in high yield and purity. His current interests include solvent extraction, iridium and rhodium chemistry and smelting.

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III.2 *Refractory Ores*

Developments in Mineral Processing, Vol. 15
Mike D. Adams (Editor)

Chapter 37

Refractory sulfide ores – case studies

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1. INTRODUCTION

There is no universally applicable programme for the evaluation and selection of a refractory ore-treatment process. Each project needs to be carefully executed in its own right. This chapter presents three examples of projects completed by GRD Minproc to illustrate this principle.

The Sansu case study highlights the amount of work and detail required to introduce what was at that time a relatively new technology, on a scale that was significantly greater than anything attempted previously.

The Kanowna Belle case study shows that, while a process route (BIOX®) may have been favoured during the earlier study phases, the final process selection was largely governed by the pilot-plant testwork and site factors such as location, water quality and water availability.

The Macraes case study is an example of flowsheet development through continuous improvement by evaluation, trialing and the use of a number of processes to address both the *preg-robbing* and refractory sulfide fractions of the ore.

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Table 1
Sansu primary ore composition

Component	Content
Gold	6–10 g/t
Sulfur	1.0–2.0%
Arsenic	0.8–1.8%

2. SANSU PROJECT, ASHANTI GOLDFIELDS CORPORATION (GHANA)

The development of the Sansu project for Ashanti Goldfields Company (AGC) has been described in a series of three papers (Nicholson *et al*., 1993, 1994a,b), detailing the selection of process route, design of the plant and its successful commissioning. The project includes a 790 tpd biological-oxidation facility, which is by far the largest commercial installation of its kind to date. In view of the success of this project, successive expansions have been undertaken, first by 33% to take concentrates from the Obuasi process plant and then by an additional 66% to facilitate increased milling capacity at Sansu.

The expansion strategy at Ashanti included a new concentrator at the southern end of the mine, initially to treat open-pit ore, followed by the treatment of ore from expanded underground operations. The ore at AGC is carbonaceous and contains significant refractory gold in association with pyrite–arsenopyrite mineralization. Typical primary ore has the composition indicated in Table 1.

The feasibility study for the Sansu project was undertaken in three phases, *i.e.*:

Phase 1: Scoping study.
Phase 2: Preliminary feasibility study.
Phase 3: Detailed feasibility studies and piloting.

The scoping study examined nine processes, including both concentrate and whole-ore treatment routes. Scoping laboratory testwork was carried out on each process, followed by preliminary capital and operating cost estimates. The purpose of this study was to select two or three processes for more detailed assessment in Phases 2 and 3. The selection criteria were based not only on the process economics, but also considered factors such as the remote location, the level of operating and maintenance skills required and the environmental aspects of treating a highly arsenical ore.

Concentrate roasting had been used at Ashanti for many years and was, therefore, considered as the benchmark for process comparisons. Pressure oxidation was selected for further examination, in view of its track record in existing operations and evidence that it offered the best overall gold recovery. However, it was considered to have the highest capital cost and to be the most challenging technology to implement in Ghana.

Two other commercialized technologies were examined, although these had not previously been used on a large scale. The first of these was biological oxidation of concentrates, which was then in operation at Fairview (South Africa) and São Bento (Brazil). It appeared to offer a relatively high recovery at low capital cost and to be an appropriate technology to implement. Whole-ore roasting was the first process used at Ashanti for treatment of refractory ores, and was attractive because of the difficulties in achieving good flotation recovery at a high concentration ratio. Whole-ore roasting with oxygen (Freeport process) was also noted to have the ability to capture and fix arsenic in the roaster bed, a major environmental advantage.

The second phase of work was planned to be carried out in sufficient detail to facilitate bankable feasibility studies. This was achievable for the flotation and roasting steps, but it was determined that confirmatory pilot-plant testing would be required for biological and pressure oxidation. During this phase, it was recognized that concentrate roasting, while well proven and having attractive economics, exhibited a higher risk due to the difficulties in achieving adequate concentrate grades for autothermal roasting. Roasting of the Sansu ores would produce up to 30,000 tpa of arsenic, too large a quantity for sale into a shrinking market. A programme of laboratory work demonstrated that the most viable route would be the impoundment of arsenic trioxide in large cement blocks. This route had not been proven on such a scale previously and, if unsuccessful, the alternative disposal routes would render the project uneconomic.

Of the other three processes, biological oxidation appeared to offer the greatest potential for optimization of process economics and recovery, but would require extensive pilot-plant testwork and would involve the scale-up of the process from 40 to over 700 tpd, a particularly risky step considering the project location.

Whole-ore roasting appeared, at that stage, to demonstrate marginally the best economics and recovery, but was deemed to require additional work to assess its applicability to the wide range of ore types encountered at Sansu and to determine its environmental acceptability.

Pressure-oxidation testwork had indicated surprisingly low levels of recovery in laboratory testwork and was also deemed to require additional testwork.

It was concluded that it would be necessary to take three processes through to a final feasibility study stage due to the uncertainties associated with the scale-up and applicability of biological oxidation and whole-ore roasting.

Pilot-plant testwork was carried out on biological oxidation, both on site, by BacTech, and in South Africa, by Genmin (now Goldfields). Additional pilot-plant testing of the oxygen roasting was also carried out, together with environmental studies that examined the stability of the arsenic in the calcine and the effectiveness of sulfur capture in the roaster bed. Further, laboratory testwork at Sherritt demonstrated a significant increase in gold recovery through the use of higher oxidation temperatures.

Capital and operating costs were developed to an accuracy of ±15%, and Table 2 summarizes the results of the Phase 3 studies.

Following these studies, AGC eliminated the option of whole-ore roasting due to the poor gold recovery and instability of arsenic in the residue. Genmin was selected as the preferred technology supplier for biological oxidation, based on the results of the pilot-plant testing and on its greater experience at that time, in the design and operation of production-scale plants.

Prior to analysis of the remaining two process routes, AGC personnel undertook an extensive tour of existing biological and pressure-oxidation (POX) plants. Table 3 summarizes the decision analysis criteria then used to select the Genmin BIOX® process for implementation, shown in Fig. 1.

The main points from the comparison were as follows:

- Despite higher overall gold recovery from pressure oxidation, the biological-oxidation route offered a significantly higher net present value (NPV).
- A delay in project start-up of at least 6 months would have occurred with the pressure-oxidation route due to the long lead time for the fabrication and installation of the autoclaves.
- The level of operating complexity for biological oxidation is significantly

Table 2
Sansu Phase 3 cost estimates and recoveries

	Capital cost (US$M)	Operating cost (US$/t)	Recovery (%)
Whole-ore roasting (excluding licence)	113	12.6	80–82
Pressure oxidation	121	15.37	93
BIOX® (Genmin)	99.8	16.85	91
Biological oxidation (BacTech)	94.9	16.85	85–89

Table 3
BIOX® vs. POX decision analysis

Objective		BIOX®		POX	
	Weight	Rating	Weighted	Rating	Weighted
Maximum gold recovery	10	8	80	10	100
Generation of best NPV	8	10	80	7	56
Commissioning by 1 April 1994	10	10	100	0	0
Simplicity of operations	8	8	64	6	48
Simplicity of maintenance	8	10	80	6	48
Flexibility of process for AGC ores	7	7	49	10	70
Environmentally acceptable	10	10	100	10	100
Safety considerations	10	8	80	4	40
Dependence on 'High-Tech' ancillaries	5	10	50	2	10
Minimize spares holdings	6	8	48	3	18
Maximize local personnel	7	8	56	3	21
Ease and cost of expansion	5	10	50	5	25
Complexity of training requirements	4	7	28	4	16
Ease of start up/shut down	5	5	25	5	25
Degree of instrumentation	3	8	24	4	12
Total		127		79	
Weighted total			914		589

Notes: Weight – On a scale of 1 to 10, the objective is ranked in order of its degree of importance to AGC, 10 being the highest. Rating – The ability of each process to achieve the objective was determined, 10 being the highest. Weighted – This is derived by multiplying the Rating by the weight.

Fig. 1. Sansu BIOX® Project.

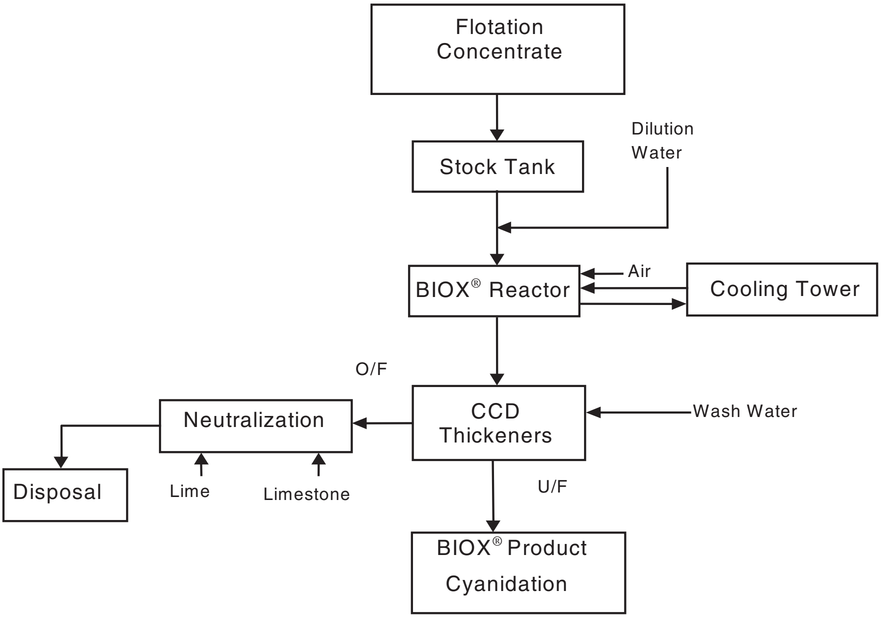

Fig. 2. BIOX® flowsheet for Sansu.

lower. This allows for easier staff training and considerably simpler logistical support. In the case of Sansu the technology required significantly fewer expatriate staff, especially during the initial phases of operation.

- Biological oxidation was conducive to cheaper future expansions.

The selection of the process route for the Sansu project (see Fig. 2) took over 2 years of exhaustive investigation. The process finally selected was, at the time of the initial studies, still in its infancy and required significant scale-up, a reflection of how rapidly technology can change in this field.

It should also be stressed that the selection of the process was highly site-specific and subject to prevailing cost structures and infrastructure.

Of particular note was the change in project ranking between the original scoping study used for preliminary process selection and the final feasibility studies. This was particularly affected by changes in overall recovery, albeit slight, predicted by testwork and by reagent consumption projections. In addition, perceptions of the environmental-mitigation steps required changed significantly during the study, especially with regard to the whole-ore roasting process. For instance, this process could have been the preferred process route if the project location had not required sulfur dioxide scrubbing and if flotation and biological-oxidation recoveries had not been improved during the final pilot-plant testwork programmes.

3. KANOWNA BELLE PROJECT (WESTERN AUSTRALIA)

Kanowna Belle represented a major new gold project located near Kalgoorlie in Western Australia. The primary ore to be treated is refractory in nature, exhibiting only 70–75% recovery, even after fine grinding and cyanidation. The ore has a low average sulfide content of approximately 1%, predominantly pyrite.

There is a severe shortage of good quality water in the Kalgoorlie area. Local groundwaters, which are used in the area for milling, have a salinity level of over 200,000 mg/L total dissolved solids (TDS) and a chloride level of 110,000 mg/L. Potable water is brought by pipeline from the coast over 600 km away. Any usage over a small initial allocation attracts a substantial capital contribution. In addition, the project location resulted in high power costs, at that time, of over A$0.12/kWh and high costs for bulk reagents such as lime.

Preliminary laboratory testwork allowed the following conclusions to be drawn:

- Gold is predominantly associated with the sulfide minerals and occurs both as minute inclusions and in micro-fractures on the outside of pyrite grains.
- Pyrite is the dominant sulfide mineral, with small quantities of arsenopyrite.
- Flotation performance is relatively consistent, giving a high concentration ratio and recovery.
- All oxidation processes tested achieved greater than 90% recovery of gold from the residue. Hydrometallurgical processes, such as biological oxidation and pressure oxidation, appeared to offer the potential for the highest recovery, with small-scale testing indicating recoveries greater than 98% from flotation concentrates.

Using the results of this work, a refractory process study was commissioned by the client. This generated ±20% capital and operating cost estimates and enabled the evaluation of the options on a technical and economic basis. The results of the analysis are summarized in Table 4.

The conclusions drawn from this study were:

- Concentrate options were superior to whole-ore roasting.
- Concentrate roasting, with sulfur-dioxide discharge, provided the most economic route. Adding the costs associated with off-gas scrubbing had a significant adverse effect on the NPV of this option.
- Biological oxidation, on an economic basis, was only marginally inferior to roasting with SO_2 discharge. Its higher capital and operating costs were largely counteracted by increased revenues from higher gold recoveries.

Table 4
Kanowna Belle project refractory process study

Process Option	Risk	Technical complexity	NPV (A$M)	Recovery (%)
Concentrate treatment				
Fine grinding				
16.7 µm	Low	Low	20.1	72.1
6.1 µm	Low	Low	31.1	78.1
Biological oxidation	Moderate	Moderate	112.7	98.9
Pressure oxidation	Moderate	High	95.8	99.1
Roasting				
SO_2 emission	Low	Low	114	93.8
SO_2 capture	Moderate	Moderate	81.4	93.8
Whole-ore treatment				
Roasting				
CFB	Moderate	Moderate	37.8	93.1
Freeport	Moderate	Moderate	43.7	nd

- Pressure oxidation was less favourable due to the high local power cost and the requirement for large amounts of high-quality water.

Based on this evaluation, concentrate roasting and concentrate biological-oxidation were selected as the preferred options for more detailed analysis. A programme of detailed pilot-plant testing and environmental and engineering studies was developed for both options.

Initial pilot-plant testing for roasting confirmed the laboratory test results of 90–91% recovery, but also indicated that, whilst significant arsenic volatilization had occurred, most had been retained in the calcine. Further testing demonstrated that two-stage roasting increased the volatilization, albeit only to 40–45%, but this was sufficient to raise the gold extraction to over 97%.

Engineering studies by GRD Minproc showed that this increase in gold recovery compensated for the additional cost of capturing and disposing of the arsenic. Studies assumed the fixation of arsenic as ferric arsenate, although it would be possible to sell the arsenic trioxide in view of the small quantities generated (250 tpa) and the relatively high purity. Additional studies demonstrated the strong potential and viability of alternative, although less proven, arsenic disposal routes.

Local legislation permitted sulfur-dioxide emissions except where it directly impacted on environmentally sensitive areas or population centres. Detailed climate and plume dispersion modelling demonstrated that strict operational guidelines, including suspension of roaster operations in the event of particular climatic conditions, would prevent an adverse impact on the local population centres. As a part of the engineering studies, a detailed examination was also undertaken of the impact on costs of sulfur-dioxide capture, either by sulfuric-acid production or by using lime to scrub the off-gases.

Batch testing of bacterial oxidation was carried out by three organizations, namely BacTech, Genmin (now Goldfields) and CRA. All achieved gold recoveries of 97–99% following oxidation in fresh water. Genmin tested the effects of salinity, at levels of 2,500 mg/L chloride, and this had no significant impact on sulfide oxidation. However, it significantly lowered the levels of gold recovery and gave rise to substantially higher lime and cyanide consumptions. This reduction in gold extraction was attributed to high levels of jarosite precipitation around the liberated gold, owing to the higher salt content.

An extensive pilot-plant programme was then undertaken by Genmin. This programme was designed to determine the design parameters for biological oxidation and to investigate alternatives to the normal BIOX® process that could result in lower water consumption, potentially the most critical factor in the economics of the process at Kanowna Belle. This pilot-plant programme and the resulting BIOX® circuit have been described in some detail by Weston *et al.* (1994). The flowsheet is shown in schematic form in Fig. 3 and its key features are as follows:

- Reduction in water consumption through filtration and recycling of neutralized liquors.
- Use of cyanide-contaminated water.
- Use of hypersaline water in reactor cooling.
- Operation at 45°C.

The pilot-plant programme also confirmed that salinity did not impact directly on the bacterial action, but rather indirectly by occlusion of the gold and sulfides through jarosite precipitation. Thus, although bacterial activity did not appear to be impaired, the oxidation rate and gold recovery were both significantly reduced at chloride levels in excess of 1.5 g/L. Although operating at lower pulp densities could have mitigated this impact and thereby reduced the jarosite precipitation, it was determined that this would result in higher costs by substantially increasing the costs of the reactors and downstream equipment.

Although pyritic sulfur oxidation was over 94%, the corresponding gold recovery was only 93–94%, a significant drop from the 97–99% predicted by batch testing in fresh water, especially when the increase in roaster recovery was considered.

Capital and operating costs were estimated in definitive feasibility studies to an accuracy of ±10%. These are summarized in Table 5.

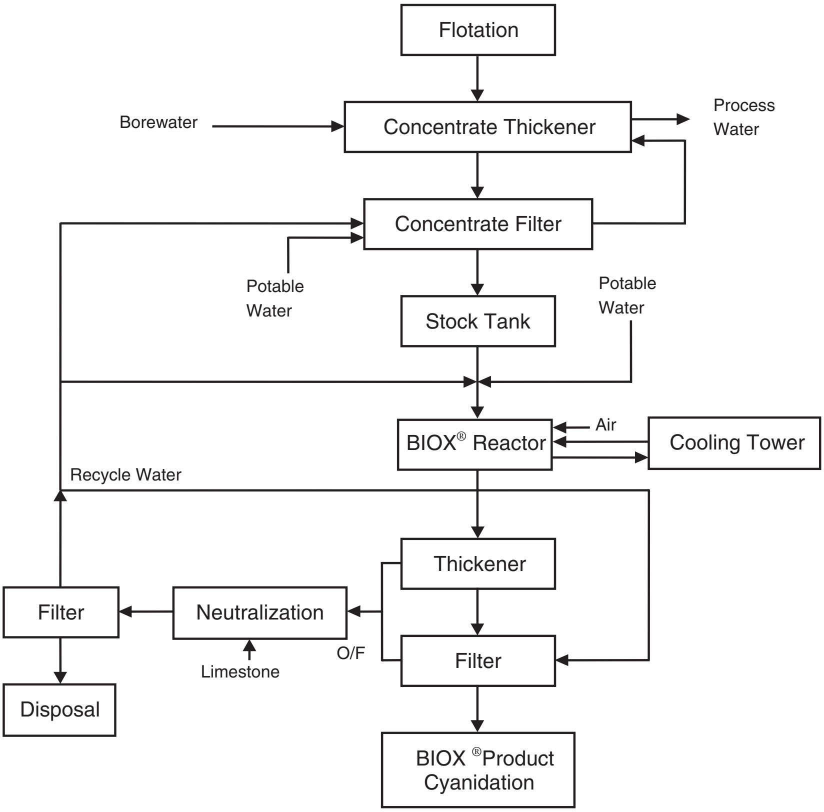

Fig. 3. BIOX® flowsheet for Kanowna Belle.

Table 5
Kanowna Belle definitive study capital and operating cost estimates

Process Option	Capital costs (A$M)		Operating costs (A$/t con)	
	Direct	Indirect	Total	
Roasting				
With SO_2 emission	27.1	7.6	34.7	86.5
Limestone scrubbing	33.5	9.3	42.8	151.2
Acid plant	42.9	8.8	51.7	113.4
Biological oxidation	37.4	11.8	49.2	168.0

Even when large contingent costs of $1.5 M for capital and $35.4/t for operating are allowed for ferric arsenate fixation in the roasting route, the biological-oxidation option is less attractive than roasting, both with and without sulfur-dioxide capture, owing to the lower gold recovery predicted in the pilot-plant testwork. However, there is significant potential for reducing these costs through sales of arsenic trioxide or alternative fixation methods.

It should be noted that the higher BIOX® capital costs were largely related to the capital charges for water supply and the higher project-management costs.

The higher operating costs were predominantly due to higher consumption of power and cyanide and the need to scrub the sulfates released in oxidation with limestone. However, the lower costs of the limestone-scrubbing option demonstrate the relative importance of the latter factor.

The prime causes for the change in the relative economics for BIOX® include:

- Lower gold recovery when oxidation was tested in saline water.
- Improvement in gold recovery through optimization of roasting conditions.
- Underestimation of the costs and difficulties associated with reactor cooling in saline conditions.
- More detailed and accurate estimation of project indirect costs.

The relative economics of the two processes at Kanowna Belle are difficult to extrapolate to other projects for the following reasons:

- The low arsenic content of the ore has a major beneficial impact on the economics of roasting due to the low disposal costs. A slight increase in the volatilized arsenic content would result in a large increase in operating costs.
- The low sulfide content and low ore throughput allowed a single conventional roaster to be used. A higher treatment rate for sulfide sulfur had the potential to significantly add costs through the need to use a CFB roaster or multiple trains.
- The high unit costs at that time for electrical power and lime in Kalgoorlie both adversely impact on BIOX®.
- The high costs associated with providing good-quality water were specific to the Kalgoorlie region.
- The clean pyritic nature of the ore resulted in a relatively flat flotation grade-recovery curve, which eliminated the advantage of BIOX® in being able to treat a bulk concentrate.

The Kanowna Belle roaster is shown in Fig. 4.

Fig. 4. Kanowna Belle roaster and arsenic bag-filter.

4. MACRAES GOLD PROJECT (NEW ZEALAND)

The Macraes Gold Project is located 60 km north of Dunedin in the South Island of New Zealand. The original treatment plant was commissioned in October 1990 and was designed to treat 1.0 Mt/a of oxide ore or 1.5 Mt/a of sulfide ore on a campaign treatment basis (Allen *et al.*, 1993).

It became clear early in the mine life that the ore was preg-robbing, but the exact nature of the preg-robber was much less clear-cut, with some form of carbonaceous material and/or fine pyrite identified as possible candidates. The highly sheared ultra-fine grained material in the hanging wall structure shows the highest preg-robbing behaviour. Attempts to characterize the preg-robbing by scanning electron microscopy, electron microprobe or laser-induced mass spectrometry have had limited success due to the fine grain-size. Transmission electron-microscopic examination of material extracted by acid digestion (Taylor, 1997) has provided evidence of very fine-grained (submicron) carbonaceous platelets, dispersed through silicates and sulfides in the highly sheared cataclasite. Research at Otago University has confirmed these conclusions, and shown that the carbonaceous extract from the sulfides and silicates behaves in a similar manner to activated carbon (Dobson and McQuillan, 1998). Hence, any technique that is to provide a significant improvement in gold recovery has to deal with sulfide encapsulation of gold in pyrite and in arsenopyrite as well as combat preg-robbing by submicron carbonaceous material.

As understanding of the Macraes orebodies has developed, the plant has gone through a number of phases of improvement and expansion as follows:

Phase 1: Expansion (2.2 Mt/a) and recovery improvements (commissioned 1992).
Phase 2: Expansion (3.0 Mt/a) (commissioned 1994).

Phase 3: Recovery enhancement (commissioned 1996–1998).
Phase 4: Recovery enhancement – flotation, pressure oxidation (commissioned 1999).
Phase 5: Expansion (4.5 Mt/a) (commissioned 2002).

Phases 1 through 3 have delivered incremental gains in recovery and lower operating costs, mainly through improvements to the flotation circuit. However, the preg-robbing components have proven to also be responsive to flotation, with cleaning having minimal impact on eliminating this material. Therefore, cycloning of the rougher and scavenger concentrates has also been introduced. Whilst there is a loss of gold in the slimes fraction, this is more than compensated for by reduction in losses through preg-robbing in CIL.

In 1996 and 1997, Macraes Mining Company Ltd planned to expand production to over 9 Mt/a through installation of a new 6 Mt/a greenfields plant, to process recently discovered extensions of the orebody. However, the collapse in the gold price in 1997 and delays in obtaining the necessary resource consents resulted in the deferment of the proposed expansion.

At the same time, continuing process evaluations had identified that Newmont Gold Company's pressure-oxidation technology held some promise for treatment of Macraes flotation concentrates. A study team, combining Macraes Mining Company and GRD Minproc personnel, was assembled to define future mining and processing options.

The evaluation considered a variety of options, including plant expansions, new greenfields plants and available process technologies. This included a reassessment of available refractory process options, not just the Newmont technology. Roasting was discounted due to environmental considerations and biological oxidation did not produce acceptable gold recoveries, as this did not address the preg-robbing component of the gold losses.

To assess the applicability of the Newmont pressure-oxidation technology, scouting tests were conducted on concentrates originally prepared for roasting testwork. Batch tests on the high-grade concentrates suggested that up to 93.5% CIL gold recovery could be obtained after pressure oxidation of highly preg-robbing float concentrate (23% S and 14% As) and up to 95.8% on low preg-robbing material (27% S and 7% As). The advantage of the technology over other process routes was that it addressed both the refractory and preg-robbing nature of the ore. This was followed by a program of semi-continuous pressure-oxidation testwork, using the technique developed by Gathje *et al.* (1995) to identify preliminary optimum conditions for continuous pilot-plant pressure-oxidation testwork. A continuous pilot-plant campaign was then conduced at Hazen Research in their four-compartment 32 L autoclave.

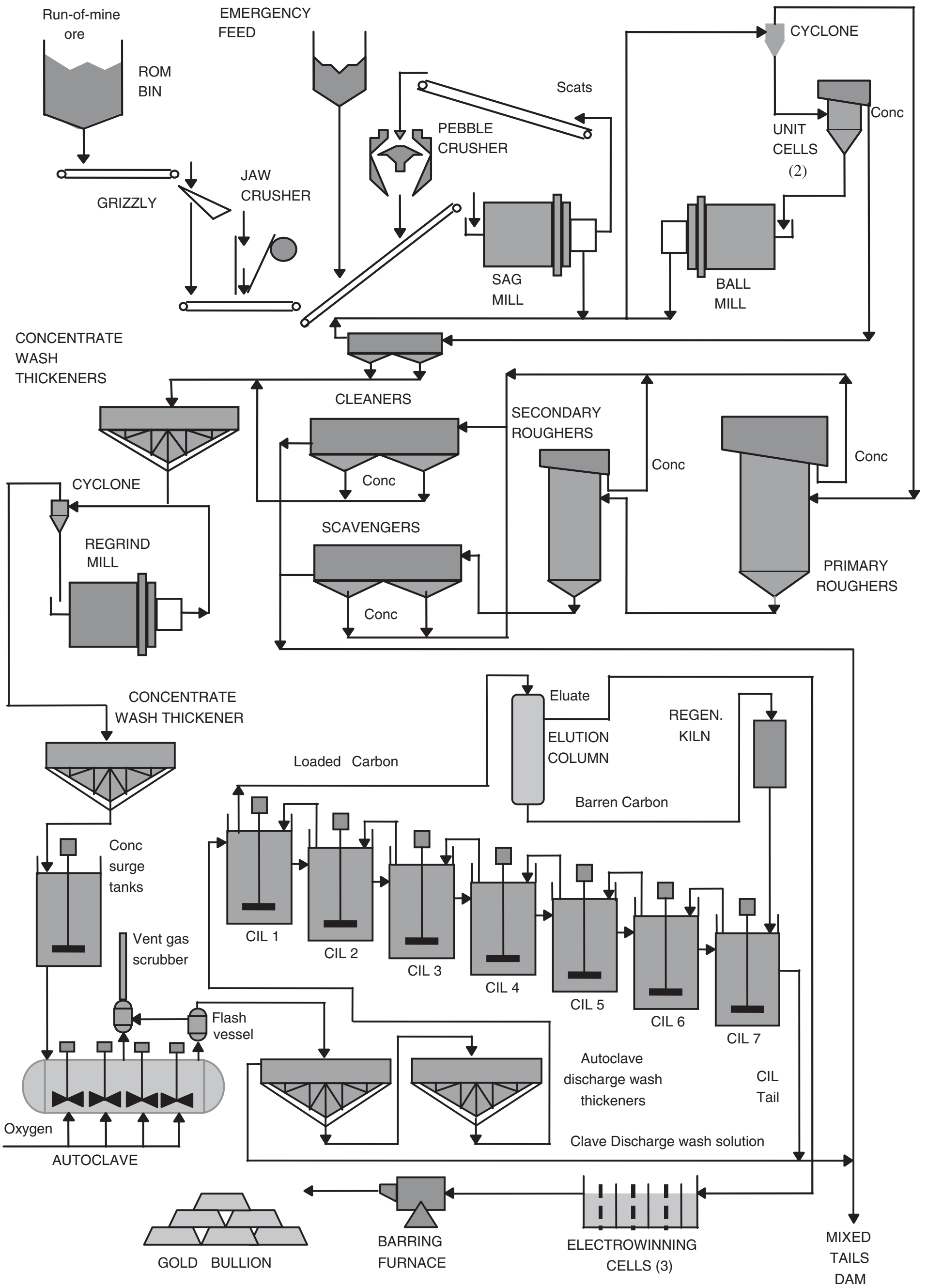

Fig. 5. Macraes Stage 1 expansion circuit.

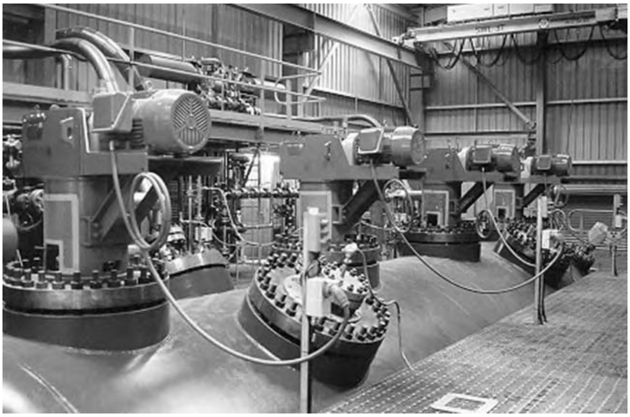

Fig. 6. Macraes pressure-oxidation autoclave.

At the end of the evaluation process a development plan was formulated, consisting of two stages of development, namely:

Stage 1:	Upgrading of milling and flotation circuits, installation of Newmont's pressure oxidation process technology and treatment of CIL residues. This is illustrated in Fig. 5.
Stage 2:	Expansion of plant capacity to 4.5 Mt/a.

The Macraes Gold Project testwork went from scouting tests, to pilot-plant scale, to engineering design within a period of a year. The pressure-oxidation autoclave at Macraes is shown in Fig. 6.

The upgrading of the milling and flotation circuits was targeted at improving recovery of sulfides in coarser size-fractions, which were being lost as the primary grind coarsened to allow increased plant throughput. Particular focus has been applied to the sub-optimal performance of the column flotation cells in these size fractions. The circuit has been reconfigured to increase the conventional cell capacity.

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David Lunt is recognized by the minerals processing industry worldwide as one of the industry's most experienced technical professionals. His career consists of 36 years of operational and consulting experience. David has worked on a wide range of major studies and projects in almost all commodities, including the management and execution of detailed designs and studies for gold (oxide and refractory), copper (oxide and sulfide), uranium, diamonds, nickel laterites and sulfides, vanadium and other minerals and metals. In addition to his technical experience, David has significant senior management experience having held a number of senior positions with GRD Minproc, including General Manager of the Company's Sydney and Teheran offices. David assumed his current position of Chief Technical Officer in 2002, and also sits on the GRD Minproc Board.

His international experience is extensive having worked on all continents. David's recent career includes consulting assignments for Rio Tinto, Anglo American and BHP Billiton. Two of his many achievements at GRD Minproc are the development of one of the industry's strongest hydrometallurgical groups and the development of business in Africa.

Nigel Briggs has 14 years experience in gold, mineral sands, nickel sulfide and nickel laterite processing, particularly in the areas of production management, engineering design and technical support. His people management skills cover a particular interest in the development of supervisory and technical personnel, along with support systems to facilitate this. He has experience in managing plants through periods of substantial change.

His experience covers the supervision of internal and external testwork, leading to justification and implementation of process changes, through design or modification, particularly the identification and improvement or elimination of issues that adversely affect safety, production or cost performance within an operating plant. He has a keen interest in the application of inherently safer design and hazard studies in engineering design.

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Chapter 38

Preg-robbing gold ores

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1. INTRODUCTION

In the case of certain ores, gold recovery by cyanidation is limited by the presence of naturally occurring carbonaceous material, which adsorbs gold from alkaline cyanide solution unless steps are taken to prevent this adsorption reaction from occurring. Such ores are most often referred to as *preg-robbing* ores. While they could be termed refractory carbonaceous ores, being refractory in the sense that gold recovery is made difficult by the adsorption losses that occur, this may be confused with cases of gold encapsulation within carbonaceous materials such as *kerogen* (solid hydrocarbons formed from deposits of spores, pollen or algae). Smith first used the term *preg-robbing* in 1968 and later it was used by others (Hausen and Bucknam, 1985; Stenebråten, 1998; Stenebråten *et al.*, 1999). It is now in common use in the gold industry. Preg-robbing is an important phenomenon, which inhibits gold recovery due to the presence of this naturally occurring carbonaceous matter. Such behaviour was detected as early as 1911 by Cowes, who found that gold losses in the tailings of the Waihi-Paerola Operation in New Zealand were due to the presence of natural carbon in the ore (Menne, 2003).

Also, it should be mentioned that a wide variety of other minerals, including copper-sulfide minerals, clay and silicates can adsorb gold depending

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on their surface area and surface characteristics. In this section, the preg-robbing behaviour is mainly correlated with the naturally occurring carbon species or carbonaceous matters in the gold ore. Some discussion of this topic is given in Section 4.

The mineralogy associated with carbonaceous gold ores can be quite variable (Afenya, 1991). The preg-robbing components of the ore are generally carbonaceous materials such as wood chips, non-carbonate carbon, or other components, particularly native elemental carbon (Rees and van Deventer, 2000). In some cases, the carbonaceous matter adsorbs the solubilized gold-cyanide complex from leach solutions, and carries the gold with the tailings, leading to poor gold recovery. This can be a very serious problem as a small amount of carbonaceous matter may adsorb essentially all of the solubilized gold due to its small particle size and porosity (Sibrell, 1991; Pyke *et al.*, 1999). Also, the gold may be occluded by the carbonaceous matter, preventing solution access (Tafuri, 1987; Sibrell, 1991).

The carbon content usually varies significantly, even in the same ore deposit. Data from some studies show ores with less than 1% to over 8% carbon content for deposits in the Carlin trend (Sibrell, 1991; Stenebråten *et al.*, 2000; Afenya, 1991). Gold losses due to preg-robbing during cyanidation of carbonaceous ores may vary from less than 20% to as much as 90% (Stenebråten *et al.*, 2000).

Carbonaceous material occurs in many deposits around the world, as shown in Table 1 (Marsden and House, 1992; Menne, 2003). They are usual components of metasedimentary rocks that are often diffused within the mineral matrix (Beyssac *et al.*, 2002). The carbonaceous material comes from the solid-state metamorphic transformation of organic material originally in contact with the rock. This transformation is called graphitization and depends on temperature, pressure and type of carbon precursor. (Beyssac *et al.*, 2002). Naturally occurring carbonaceous material is found in many sediment-hosted disseminated gold deposits, like the famous Carlin trend (northeastern Nevada, USA). Two scanning electron microscope (SEM) micrographs of a commercial activated carbon and a carbonaceous material from a Carlin trend ore are shown in Fig. 1. The SEM A-micrograph shows a quite uniformly macroporous surface for a commercial activated carbon. The SEM B-micrograph shows an amorphous pore structure for the carbonaceous matter isolated from the ore. This carbonaceous material (CM) had a carbon content of 40%, a surface area of 42.7 m^2/g CM and a gold-adsorption capacity constant of 2200 mg Au/kg CM. This type of carbon accounts for the sequestration of gold during cyanide leaching. (Stenebråten *et al.*, 2000).

The most renowned examples of carbonaceous ores, in addition to the Carlin trend (USA), are the Ashanti trend (Ghana), Witwatersrand (South Africa), Muruntau (West Uzbekistan), Kumtor (Kyrgyzstan) and Macraes

Table 1
Carbonaceous gold deposits with preg-robbing characteristics (modified from Menne, 2003)

Africa

- Agnes, South Africa
- Ashanti, Ghana
- Athens, Uvuma, Zimbabwe
- Barbrook Mine, South Africa
- Beatrix Gold Mine, South Africa
- Bibiani, Ghana
- Bogosu, Ghana
- Crown Mines, South Africa
- Evander Gold Mine, South Africa
- New Consort, South Africa
- New Machavie, South Africa
- President Brand, South Africa
- Prestea, Ghana
- Randfontein Cooke, South Africa
- Renco, Zimbabwe
- Samira, Niger
- Sheba, South Africa
- Sansu, Ghana
- Tarwa, Ghana
- Twangiza, Uganda
- West Rand Black Reef, South Africa
- Worcester, Barberton, South Africa

North America

- Alligator Ridge, NV, USA
- Atlas Gold Bar, NV, USA
- Betz, NV, USA
- Big Springs, NV, USA
- California Mother Lode, CA, USA
- Carlin Gold Mine, NV, USA
- Cortez Gold Mines, NV, USA
- Deep Star, NV, USA
- Donlin Creek, Alaska, USA
- Enfield Bell, NV, USA
- Eskay Creek, NV, USA
- Getchell, NV, USA
- Gold Acres, NV, USA
- Gold Quarry, Carlin, NV, USA
- Goldstrike, NV, USA
- Gordon Lake, Canada
- Jerrit Canyon, NV, USA
- Kerr-Addison, Canada

Table 1 (*continued*)

McDermott, Ontario, Canada
McIntyre Porcupine, Canada
McLaughlin, CA, USA
Maggie Creek, NV, USA
Mercur, UT, USA
Mother Lode, Canada
Ochali, B.C., Canada
Post, NV, USA
Queen Charlotte Island, B.C., Canada
Royal Mountain King, CA, USA
Turf, NV, USA
Turquoise Ridge, NV, USA
Zortman, MO, USA
Australia/Asia
Bakyrchik, Kazakhstan
Cosmo Howley, Australia
Fosterville Gold Project, Australia
Fortnum, Australia
Gympie, Australia
Hedges, Australia
Jundee, Australia
Kelian, Indonesia
Kumtor, Kyryzstan
Macraes, New Zealand
Moline, Australia
Muruntau, Uzbekistan
Nimary, Australia
Paddington, Australia
Penjom Mine, Malaysia
Porgera, Papua New Guinea
Stawell Gold Mine, Australia
Tanami, Australia
Temora, Australia
Waihi/Paeroa, New Zealand
Central/South America
Alto Chicama, Peru
Esquel Gold, Argentina
Las Cristinas, Venezuela
Morro do Ouro, Brasil
Morro Velho, Brasil
Pueblo Viejo, Dominican Republic
Rosario Dominicana, Dominican Republic
San Nicolas, Peru
Santa Barbara, Huancavelica, Peru

Table 1 (*continued*)

Elsewhere
Kyuchus, Russia
Natalinsk, former USSR
Nezhdaninskoye, Russia
Salsigne, Orleans, France
Ternei District, Primorski Krai, Russia

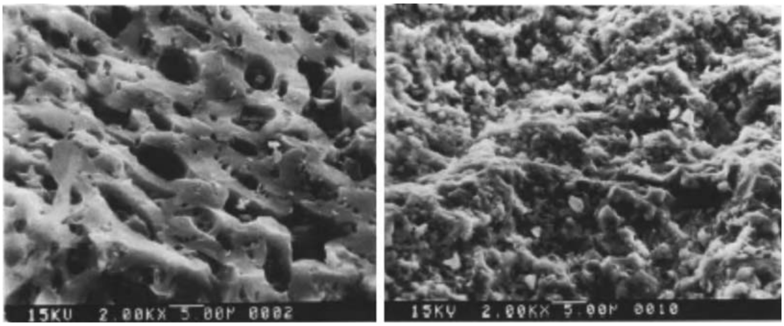

Fig. 1. SEM micrographs of a commercial activated carbon and a carbonaceous material from a Carlin trend ore (courtesy of Dr. Stephen Chryssoulis).

(New Zealand) (Varshal *et al.*, 1995; Rogers, 2004; Cadzow and Giraudo, 2000). There are also various Western Australian deposits (Menne, 2003; Marsden and House, 1992). New deposits both in the exploration and exploitation stages include in Argentina (Minesite.com. 2000), Perú (Barrick, 2003; Noble and Vidal, 1990; Slaughter, 2004), Malaysia (Avocet Mining, 2004), Australia (Pyke *et al.*, 1999), Laos (Pan Australian Resources, 2003), Alaska, USA (McClelland, 2001), Russia (Celtic Resources, 2004; Grigg and Dorey, 2002; Whidden, 1997), Venezuela (Goode and Thomas, 2004), Fast East Russia (Hausen, 2000), and Niger (Parkgreen Communications, 2003). These examples show that carbonaceous gold deposits are found around the world.

The presence of carbonaceous matter in an ore does not necessarily result in poor gold recovery (Sibrell, 1991; Stenebråten, 1998). It seems that carbon can exist in different forms in the ore, which show different affinities for the gold-cyanide complex. (Stenebråten, 1998). Native carbon in a carbonaceous ore is believed to behave similar to activated carbon when in contact with aurocyanide solutions (Sibrell, 1991; Wan and Miller, 1990; Pyke *et al.*, 1999).

To help geologists to classify ore deposits, the preg-robbing gold analysis (see Section 6) has been used extensively to characterize preg-robbing behaviour of gold ores. Raman spectroscopy has been successfully used to characterize and predict preg-robbing behaviour for carbonaceous refractory ores (Nelson *et al.*, 1982; Beyssac *et al.*, 2002; Staunton, 2004).

2. CARBONACEOUS MATTER AND GOLD ADSORPTION

2.1. Chemical characteristics

Carbonaceous matter in a gold ore has been shown to act like activated carbon and adsorb solubilized gold from cyanide solution during leaching. It is thought that the dispersion of the carbonaceous matter and its fineness (less than 20 μm) account for the high adsorption and loss of gold during cyanidation (Sibrell and Miller, 1991; Pyke *et al.*, 1999).

The most studied preg-robbing ores are those from the Carlin trend (Nevada, USA). According to Rees and van Deventer (2000), this carbonaceous ore has kerogen as the principal preg-robbing component. Working with shale material containing natural carbon, van Vuuren *et al.* (2000b) also found a kerogen material in a South African ore, which was similar to kerogen of the Witwatersrand conglomerates (van Vuuren *et al.*, 2000b). In contrast, results from other studies seem to indicate that the carbonaceous matter is mostly aromatic with an activated carbon-type structure, similar in maturity to anthracite-grade coal (Sibrell *et al.*, 1990; Stenebråten *et al.*, 1999).

Radke and Scheiner (1970), apart from carbonates, separated the carbonaceous material in refractory gold-bearing ores into three components (Sibrell *et al.*, 1990; Pyke *et al.*, 1999):

- a native carbon component capable of acting like activated carbon and therefore able to adsorb gold-cyanide complexes from solution;
- a heavy hydrocarbon mixture of a high molecular weight usually associated with the native carbon component and which does not appear to adsorb gold, and
- an organic acid, similar to *humic acid*, containing functional groups capable of complexing with soluble gold to form gold–organic complexes.

Nelson *et al.* (1982) have found the activated carbon structure in a Carlin ore but not the hydrocarbon or humic acid carbons. Hatcher *et al.* (1985) found that carbonaceous matter isolated from a Carlin ore was composed of aromatic structures, essentially similar to anthracitic coal. Sibrell *et al.* (1990), working also on Carlin ores, found very low concentrations of hydrocarbons but no humic acids present in the ore. Stenebråten *et al.* (1999) did not find any detectable amounts of hydrocarbons in the Barrick Goldstrike ore. Tafuri (1987) did not find any humic acid in Mercur ore; the carbonaceous matter found was mostly aromatic with an activated carbon-type structure, similar in maturity to anthracite-grade coal (Sibrell *et al.*, 1990, Stenebråten *et al.*, 1999). Osseo-Asare and co-workers (Osseo-Asare *et al.*, 1983; Abotsi and Osseo-Asare, 1986, 1987), working with a carbonaceous gold ore from Prestea Goldfields (Ghana), were able to separate activated carbon and hydrocarbon fractions, but found no humic acids.

More recent studies have confirmed no detectable amounts of humic acids or hydrocarbons in either high or low preg-robbing carbonaceous material from Barrick Goldstrike Mine (Carlin trend, Nevada). Rather, it was found that the carbonaceous material consisted of relatively featureless aromatic structures forming an activated carbon or graphite-type matrix with ether or thiocarbonyl functionality (Stenebråten *et al.*, 1999; Schmitz *et al.*, 2001a).

According to the study of Pyke *et al.* (1999), the addition of hydrocarbons (*n*-alkanes) or carbonate carbon to the ore does not affect the gold recovery by cyanidation. Hydrocarbons have been investigated and have been reported to improve gold recovery, as the hydrocarbons coat the native carbon thus reducing its ability to adsorb gold (Guay and Peterson, 1984). However, in their study, Pyke *et al.* (1999) found that the presence of hydrocarbon had little influence on gold recovery.

Pyke *et al.* (1999) also added 0.25% humic acid to an oxidized ore that reduced gold recovery by 1%, which is not particularly significant. In that study, organic carbon similar to humic acid material (*i.e.*, humic/fulvic acid) was not detected in the sulfide ore, but a fulvic-acid extract was recovered from the concentrate and constituted 0.09% of the ore.

The addition of native carbon to an oxidized ore produced a detrimental effect on gold recovery, decreasing the recovery by about 20%. This native carbon was not as effective as commercial activated carbon in gold adsorption (Pyke *et al.*, 1999).

One important point that has been made in recent years is that the carbonaceous material is "relatively featureless with no indication of carboxylic, phenolic or hydryl functionality" (Stenebråten *et al.*, 1999). Stenebråten *et al.* (1999) suggested that the controversial $1250\,\mathrm{cm}^{-1}$ peak found in spectroscopic analysis of Goldstrike carbonaceous matter may be an ether or a thiocarbonyl functionality. Sulfur was detected to be present in this carbonaceous matter, which supports the possibility of a thiocarbonyl-type structure in the Goldstrike carbonaceous material (Stenebråten *et al.*, 1999).

The comparison between Fourier-transform infrared spectroscopy (FTIR) spectra of the carbonaceous matter and commercial activated carbon that has been activated at temperatures above 750°C (Adams, 1989) confirms the remarkable similarity between these materials, which implies that they are "chemically equivalent" (Stenebråten *et al.*, 1999; Sibrell *et al.*, 1990; Abotsi and Osseo-Asare, 1986; Osseo-Asare *et al.*, 1983; Scheiner *et al.*, 1971;

Nice, 1971; Radke and Scheiner, 1970; Leaver and Woolf , 1930; Dorfman, 1922; Feldtmann, 1915).

Using an electron microprobe, Stenebråten *et al.* (1999) did not find any correlation between O/C atomic ratio and preg-robbing characteristics. All the O/C values were low, as expected for mature carbons.

There has not been much research done recently regarding surface-chemistry issues. Abotsi and Osseo-Asare (1986) measured the *isoelectric point* (*iep*) of carbonaceous material from Prestea gold ore and found it to be 2.7. This carbonaceous material is negatively charged between pH 3.5 and pH 11, presumably due to the presence of –OH groups at the carbon surface.

2.2. Adsorption phenomena

Previous research has shown that all carbons with a graphitic structure, regardless of porosity, adsorbed gold to some extent (Sibrell, 1991). Gold is not adsorbed to any significant extent by diamond (Miller and Sibrell, 1991). The primary factors that determine gold adsorption by carbon seem to be the graphitic structure and surface area (Sibrell, 1991; Miller and Sibrell, 1991). As expected, gold adsorption increases with an increase in surface area (Sibrell, 1991; Stenebråten *et al.*, 2000). In the case of natural carbonaceous material that was prepared from the Goldstrike deposit, surface areas varying from 1.5 to 43.8 m^2/g and corresponding to between 2.46% and about 69% carbon content were measured for 16 samples (Stenebråten *et al.*, 2000). Abotsi and Osseo-Asare (1986) working in a Prestea ore sample measured 30.2 m^2/g for a 4.56% carbon content, while Sibrell (1991) correlated the carbon content with surface area and the gold-adsorption-capacity constant (*K* value), showing that a material containing ~12–40% carbon had a surface area which varied from 25 to 42.7 m^2/g and a corresponding adsorption capacity of 330–2200 mg Au/kg carbon. These studies also showed that an increase in the carbon content of the ore increases the gold losses (Sibrell, 1991; Stenebråten *et al.*, 2000). However, surface area is not the only factor that determines adsorption capacity.

Sibrell and Miller (1992) suggested that some type of non-site-specific chemical bond is formed in gold adsorption, similar to what has been postulated to occur during gold adsorption from cyanide solution by carbon black or commercial activated carbon (see Chapter 23). Results in this research suggested that some adsorption sites are preferred over others and that these sites are directly related to the surface area.

Other fundamental studies have suggested that the natural carbon is a combination of amorphous and graphitic structure (Afenya, 1991; Adams and Burger, 1998b). Between the amorphous and graphitic structures, there is a range in maturity, which is indicated by an increase in the size of the graphite crystallites in the carbon material. With maturation, functional group content in the organic material is reduced and the crystalline structure becomes more ordered. Graphite is the final maturation product, with hexagonal unit cell structures (carbon rings) and interlayer spacing (*d*-spacing) of about 150 Å (Adams, 1989; Stenebråten *et al*., 2000).

Some authors agree that graphite, commercial activated carbon and mature naturally occurring carbonaceous material are composed of stacked sheets of aromatic carbon rings cross-linked in a random manner. It seems that the micropores of activated carbons are mostly slit-shaped spaces of less than 2 nm between twisted aromatic sheets. These sheet structures are known as *microcrystallites* or *crystallites* (Sibrell, 1991; Adams, 1989; Bansal *et al*., 1988; Schmitz *et al*., 2001a, b; Stenebråten *et al*., 2000). The maturity of the carbon is directly related to the dimension of the microcrystallite perpendicular to the aromatic planes (*Lc*), and inversely related to the atomic distance between the aromatic sheets (*d*-spacing) (Schmitz *et al*., 2001a). The adsorption of aurocyanide complexes by commercial activated carbon has been detected to be inversely related to the microcrystallite parameter *Lc* and directly related to the microcrystallite *d*-spacing (Schmitz *et al*., 2001a; Adams, 1989). Adams (1989) reported an *Lc* value of 6.9–12.3 Å for microcrystallites in a commercial activated carbon. Stenebråten *et al*. (2000) found values of 30–88 Å for a high preg-robbing ore, while higher *Lc* values (117–372 Å) comparable to 150 Å for graphite (Adams, 1993) were established for a low preg-robbing ore.

Using X-ray diffractometry, Adams (1989) determined an average *d*-spacing of 3.7 Å for commercial activated carbon having a high affinity for the aurocyanide complex. The same behaviour occurs for carbon from the preg-robbing Goldstrike ores according to Schmitz *et al*. (2001a) and Stenebråten *et al*. (2000), who reported a value of 3.5 Å for the *d*-spacing of a high preg-robbing Goldstrike ore, while a lower *d*-spacing value (3.36 Å) similar to graphite (3.349 Å) (Mantell, 1968) was determined for a low preg-robbing Goldstrike ore.

Stenebråten *et al*. (2000) and Schmitz *et al*. (2001a) found a close to linear correlation between microcrystallite *d*-spacing, percentage of preg-robbing in parent ore and carbon content for the Goldstrike ore, which indicates that the extent of graphitization has a strong inverse correlation with gold losses in the cyanidation process. The higher the crystalline maturity, the lower the preg-robbing properties in the ore. However, it is evident that some graphitization is necessary and, as discussed below, adsorption depends on the availability of edge defects in the crystal lattices.

The extensive porosity of activated carbons has a great effect on gold adsorption, particularly those highly microporous carbons with pore diameters of about 20 Å. Pore size vs. area distribution studies for Carlin carbonaceous material (Sibrell, 1991) showed a higher pore size for the carbonaceous matter (40 Å) than for activated carbon. Stenebråten *et al.* (2000) found lower total pore volume for high preg-robbing samples, ranging from 0.13 to 0.17 cm^3/g in comparison to activated carbons that range from 0.48 to 1.76 cm^3/g (Adams, 1989). However, low preg-robbing samples showed higher pore volume (0.25 to 0.31 cm^3/g) than the high preg-robbing ores, which indicates that this is not a good parameter for comparison. Miller and Sibrell (1991) suggested an inverse correlation between gold adsorption and micropore size for different carbons, varying from *microporous* (less than 20 Å) for activated carbon to *macroporous* (over 500 Å) for graphite, consistent with the results of Stenebråten *et al.* (2000), that showed an average pore diameter of 257–314 Å for high preg-robbing ores, significantly lower pore diameters than those for low preg-robbing ores (519–1050 Å).

Wet ball-mill grinding of carbonaceous ore (Stenebråten *et al.*, 2000) showed that the microcrystallite dimensions, *i.e.*, thickness (*Lc*) and length (*La*) were not affected, while average pore size, total pore volume and BET surface area suffered some variation, probably due to the breakdown of macroporosity sites.

In general, gold adsorption by natural carbonaceous matter present in an ore is believed to be due to the activated carbon type of compounds and gold adsorption is similar to that which occurs with man-made activated carbon typically used for gold recovery by industry. In this regard, gold adsorption by activated carbon from alkaline solution has been studied extensively. It has been proposed that the combined effect of electrostatic and chemical interaction between the gold-cyanide anion and the carbon surface results in the gold adsorption. Another mechanism is the ion-pair adsorption reaction, where gold is adsorbed onto the carbon surface as the neutral ion pair $[M^{n+}][Au(CN)_2^-]_n$.

From a fundamental point of view, activated carbon has a disordered microcrystalline structure, similar to graphite. The random organization of graphite microcrystals and oxidation during activation creates a porous structure, which accounts for the high surface area of activated carbon and its notable adsorptive capacity. A significant amount of research has been carried out to explain the mechanism of gold adsorption by activated carbon, the nature of the adsorption sites, and the role of specific surface functional groups in gold adsorption (Adams, 1989; McDougall *et al.*, 1980; McDougall and Hancock, 1981; Jones *et al.*, 1989a–c; Ibrado and Fuerstenau, 1992; Sibrell and Miller, 1991, 1992; Lagerge *et al.*, 1997, 1999).

Currently, the most accepted theories regarding the mechanism of gold adsorption include the adsorption of ion pairs $M^{n+}[Au(CN)_2^-]_n$ onto active sites of activated carbon. This ion-pair adsorption process is somewhat selective due to the structure of the aurocyanide anion, which is considered to be less hydrated than other cyanoanions. On this basis, the selective solvent extraction of gold from alkaline cyanide solutions has been previously explained (Mooiman and Miller, 1984, 1986; Miller *et al.*, 1987). In addition, some adsorption of the unpaired anion $Au(CN)_2^-$ occurs through electrostatic interactions at highly active sites of activated carbons that have appropriate polarity (Lagerge *et al.*, 1997, 1999). In terms of the adsorption sites, the most accepted theory suggests that gold is adsorbed at the edge or defect sites rather than at sites on the basal planes (Sibrell and Miller, 1991, 1992; Lagerge *et al.*, 1999). Regarding the role of surface functional groups on adsorption by activated carbon, researchers suggest that the presence of basic surface functional groups, specifically the pyrone type, favours the adsorption of gold onto activated carbon (Papirer *et al.*, 1987, 1991, 1995; Polonia-León *et al.*, 1993).

In 1992, Sibrell and Miller clearly showed that adsorption occurs at the edges (defects) of graphite crystals and that adsorption on the basal plane face of the crystal was insignificant by comparison. This was demonstrated from autoradiographs as shown in Fig. 2 and Table 2.

These results were later confirmed by *in situ* scanning tunnelling microscopy in 1998 (Poinen *et al.*, 1998). It is evident that site-specific adsorption is prevalent in the adsorption of gold by graphitic carbons (graphite, carbon black and activated carbon), and most of the favoured sites are at edge defects in the graphite crystal structure. Other researchers (McDougall *et al.*, 1980) have hypothesized that the adsorption of the gold-cyanide complex is due to ion exchange under conditions of low ionic strength, and to ion-pair adsorption at high ionic strengths.

It is likely that both of these mechanisms take place at edge defects in the graphite structure. Ion exchange would take place with functional groups that would be found at graphitic carbon edges. For adsorption of ion pairs, van der Waals forces would be involved, and the unsymmetrical distribution

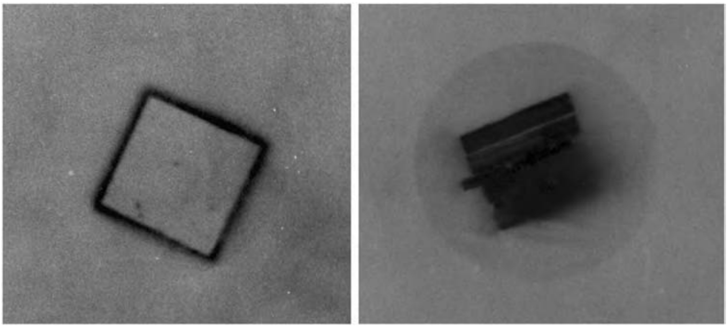

Fig. 2. Autoradiographs of highly organized pyrolytic graphite (HOPG) basal plane and edge samples after contact with radiolabelled gold-cyanide solutions.

Table 2
Gold adsorption densities as calculated by Carbon-14 radiolabelling

Sample	Adsorption density (mol/cm^2) × 10^{10}
Inert materials	
Glass	0.3
Glass (rinsed)	0.2
Silica	0.5
PTFE	0.3
Basal plane HOPG	
After equilibration	0.8
Rinsed overnight	0.7
Edge HOPG	
After equilibration	20
Rinsed overnight	10
Polished	20

of charge at edge defects in the graphite structure could well play a role in the adsorption process.

It may also be that the adsorbed complex is stabilized by attachment to more than one plane on the carbon. Although this would not be possible on the flat basal-plane surface, it could be achieved at three-dimensional edge defects in the crystal structure. These cavities created by edges would accommodate or, in effect, *solvate* the ion pair. This important phenomenon has been identified for activated carbon (Sibrell and Miller, 1991; Adams *et al.*, 1987b), for solvent extraction (Wan and Miller, 1990; Miller *et al.*, 1987; Mooiman and Miller, 1991; McDougall *et al.*, 1987; Adams *et al.*, 1987a, 1990) and for resin adsorption reactions (Akser *et al.*, 1986; Adams *et al.*, 1987b).

These graphite edge-sites or defects in activated carbons and in natural carbonaceous matter are expected to form at high temperatures and a suitable oxidizing potential. For example, defect pits, or *nanocorrals*, form spontaneously on graphite surfaces, an example of which is shown in Fig. 3 for highly organized pyrolytic graphite (HOPG) (Zhu *et al.*, 2001; Paruchuri *et al.*, 2003). These pits vary from 2 nm to several microns in size and it seems that such cages could easily accommodate the aurocyanide ion-pair adsorption reaction.

Finally, it is interesting to note that Dimov *et al.* (2003) studied the speciation of 16 different gold compounds involving halogen elements (Cl, Br, I) as well as cyanide, thiocyanate and thiosulfate using several surface-sensitive microbeam techniques, such as TOF-SIMS (time-of-flight secondary-ion mass spectrometry), TOF-LIMS (time-of-flight laser-ionization mass spectrometry)

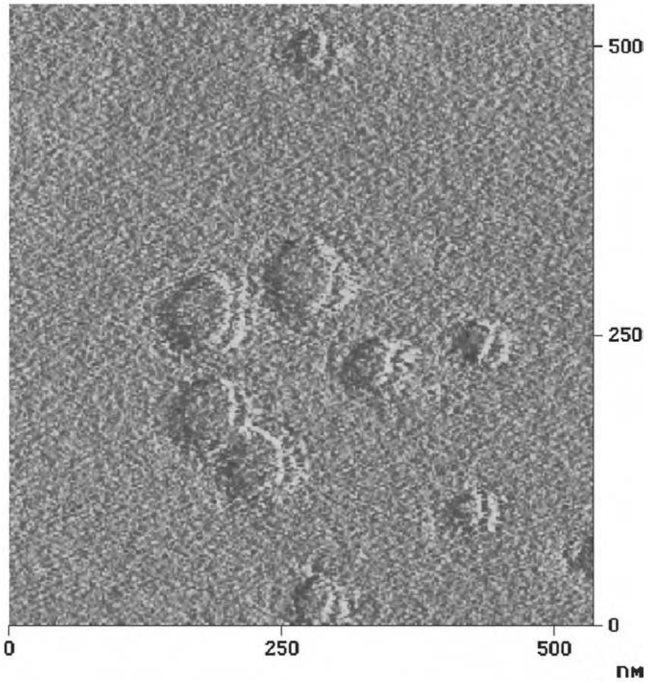

Fig. 3. Edge defects on graphite (HOPG) created by ion bombardment using TOF-SIMS at 650°C in ambient air.

and XPS (X-ray photoelectron spectroscopy). The following step in this research was to study the behaviour of the 16 gold compounds after being adsorbed by activated carbon. They found that complex gold halides when adsorbed on carbon are reduced to Au^0, which agrees with the work of Hiskey and others (Hiskey *et al.*, 1990; Hiskey and Qi, 1991, 1993). Gold cyanide coincided with $Au(CN)_2^-$ speciation, thiocyanate is reduced to $Au(SCN)_2^-$ and thiosulfate is not adsorbed onto carbon to any significant extent.

Carbonaceous preg-robbing tailings were quantified using positive-ion TOF-LIMS. Results confirmed that the increase in chloride concentrations in solution from 50 to 250 mg/L increased by five times the concentration of gold adsorbed by the carbonaceous material, thus increasing gold losses as discussed by Simmons *et al.* (1998).

3. TREATMENT OF CARBONACEOUS ORE

The preg-robbing of carbonaceous ore may be overcome using different techniques, including use of gold adsorbents (activated carbon or resins) to compete with the carbonaceous material, deactivation/passivation by oxidation (roasting, chemical and biochemical oxidation) (Sibrell, 1991; Afenya, 1991), or use of surface-blinding agents. Oxidative treatments are the most effective processes at this time. Of course, the mineralogy of the ore and the specific characteristics of the carbonaceous material must be considered to determine the most appropriate method(s) for treatment.

3.1. Activated carbon-in-leach (CIL) and resin-in-leach (RIL)

In these cases a stronger adsorbent for gold cyanide is used to compete with the carbonaceous material in the ore such as activated carbon or resin (Afenya, 1991).

The efficiency of the activated carbon used to compete with the naturally occurring carbonaceous material depends on its gold-adsorption capacity, which may be two orders of magnitude higher than that of the natural carbonaceous matter (Sibrell, 1991). In a mildly carbonaceous Carlin ore, around 70% of the gold was recovered using a CIL process in comparison with 15% gold recovery without activated carbon (Afenya, 1991).

In general, utilization of anion-exchange resins or granular activated carbon in cyanidation of preg-robbing ores improves the gold extraction but depends on ore mineralogy and the amount of adsorbents added.

One important matter of concern in the case of CIL is the carbon losses because of the duration of the process (~18 h). The normal granulated carbon (3.35 × 1.7 mm) used in CIL plants is under constant stress from contact with quartz particles from the ore. This stress causes attrition and produces gold-loaded fine-carbon particles that will carry the adsorbed gold to the tailings, exactly as the carbonaceous matter does. Adams and Burger (1998a) presented evidence suggesting that adsorbed gold on fine carbon is lowered considerably owing to re-equilibration with activated carbon granules.

One alternative under research over the past 10 years is the use of powdered magnetic activated carbon (MAC) (Miller *et al.*, 2004; Duyvesteyn *et al.*, 2002), which has a higher gold-adsorption rate than the granular activated carbon because of its smaller size (~100 μm) (Munoz *et al.*, 2003a–c). The problem of gold losses by attrition is avoided since the MAC is already powdered, so it can stay for an extended time in the pulp, to be separated at the end of the process by magnetic separation. High extents of magnetic recovery exceeding 99% of the gold loaded-MAC have been reported. (Munoz *et al.*, 2002). The higher gold-adsorption rates are important, particularly for ores with high total-carbon content. The addition of MAC in the CIL process could significantly enhance the total gold recovery in cyanidation plants. The potential advantages are that MAC reduces the possibility of gold adsorption by carbonaceous matter due to the rapid rate of gold adsorption by MAC. Further, the magnetic properties of MAC can be used to recover the normal gold losses caused by the attrition of granular-activated carbon.

Resin-in-leach (RIL) uses ion-exchange resins in direct contact with the cyanidation pulp to recover gold. Even though resin-in-pulp (RIP) has been used in the former Soviet Union for decades, there have been few applications in the rest of the world. Resins have some advantage over activated carbon, particularly the high specificity for adsorption/elution of desired compounds as well as a high loading capacity and kinetics. Normally, the higher cost compared with activated carbon and the low resilience to breakdown during processing are the most important disadvantages (Wan and Miller, 1990). The success of the RIL depends on the aggressiveness of the preg-robber (Green *et al.*, 2002). One important advantage of the RIL process over CIL is the possibility to use blinding agents in combination with resin to treat a highly preg-robbing ore. Resins are not easily fouled with organic compounds so they maintain high gold extraction performance in the presence of organic blinding agents (Green *et al.*, 2002).

Nowadays, new resins in the market, such as T-49P from Thermodyne Systems or Clean-IX® Gold from ResiX or the Minix and AURIX® resins developed by Mintek seem to have better features and performance as well as a more competitive cost. The guanidine-based resin AURIX® from Cognis seems to be more selective in CIL vs. RIL comparisons in ammonia-cyanide leaching (Mackenzie *et al.*, 1995; Yernberg, 1997; Gray *et al.*, 2000). It is interesting to mention Minix resin, which is currently being used in a gold plant in Malaysia since 1999, demonstrating excellent performance for treatment of the preg-robbing ore (Green *et al.*, 2002). This resin is also being used at the Barbrook Mine in South Africa since 2002 (Anonymous, 2003). The RIP option is discussed in more detail in Chapter 25.

3.2. Blinding or blanking

Certain chemical reagents passivate the carbonaceous matter by what seems to be selective adsorption or wetting of the carbon surface (Afenya, 1991). The blinding technique has been found to be only partially effective (Scheiner, 1987).

Adams and Burger (1998b) working on a carbonaceous shale ore, tested 16 different surfactants and oils, and also combinations of them, trying to cover a wide range of properties such as ionicity, water solubility, emulsification effects, molecular weight, aromaticity and dispersion of oil in surfactants. Different concentrations of reagents, carbonaceous material, and gold were tested. They found that most reagents required high concentrations (~1%) to affect the activity of the natural carbon, probably by completely wetting the carbon particle. Carboxy-methylcellulose or Totanin (tannin) did not affect the carbon presumably because of their very large size and hydrophilic functional groups. A long-chain *poly*oxyethylene (NP10) was the only reagent that produced any effect at low concentrations (10 mg/L). Sodium lauryl sulfate and petroleum sulfonate along with NP10 and a NP10/kerosene emulsion were the most promising reagents at dosages of about 500 mg/L. None of these blinding reagents produced a gold recovery over 75% for the carbonaceous shale ore.

Newmont Metallurgical Services has carried out tests for the passivation of a North America coconut carbon, using 26 different chemicals, inorganic as well as organic. According to the results, 12 of these reagents passivated the carbon to some extent: ammonium *per*sulfate, hydrogen peroxide, boric acid, guanidine nitrate, *tri*ethanolamine hydrochloride, potassium permanganate, potassium *di*chromate, sodium hypochlorite, chromic acid, humic acid, oleic acid, and recycled motor oil. The last six provided sufficient blinding that gold recoveries with cyanide were 50% or higher. Also, when combining the blinding passivation pretreatment with a CIL process for two high preg-robbing ores from Gold Quarry, it was found that the gold recovery increased from 13.5% to 70.5% and from 4.2% to 67% using motor oil. Further tests using azo dyes such as Alizarin Yellow GG and Mordant Orange (sodium salt of nitrophenylazo salicylic acid) as blinding agents improved gold recovery to 86% and 79% respectively (Acar and Ball, 1989).

Earlier studies regarding blinding of preg-robbing carbonaceous materials indicated that both flotation reagents (xanthates, pine oil) and non-polar hydrocarbons as diesel, light oil, fuel oil and kerosene could be used. Also, lauric acid salt, soap and soap by-products (myristic, stearic and palmitic acids salts), RV-2 (*p*-nitro-benzol azo salicylic acid) have been reported to have a blinding effect (Menne, 2003; Afenya, 1991).

3.3. Roasting

The roasting technique has been shown to be the most suitable procedure to destroy carbonaceous materials as well as to oxidize the sulfides normally associated with the ore and is widely applied (Afenya, 1991; Fernández *et al.*, 2000). Roasting temperatures of less than 600°C are common, which oxidize the carbonaceous matter and sulfide minerals in the ore:

$$C + O_2 \rightarrow CO_2 \tag{1}$$

$$2MS + 3O_2 \rightarrow 2MO + 2SO_2 \tag{2}$$

Selection of roasting temperature depends on ore mineralogy, the roasting method and specific operating conditions, such as particle size and gas flow.

A problem associated with some carbonaceous ores has been the presence of mercury and arsenic, which are of environmental concern. Improvement in scrubbing techniques for mercury and SO_2 removal (Scheiner, 1987) as well as two-stage roasting may help to control the release of gaseous arsenic compounds.

3.4. Chlorination

In the late 1960s the U.S. Bureau of Mines recognized that aqueous chlorination could be used to destroy carbonaceous material (Afenya, 1991). Gaseous chlorine (Cl_2) and sodium or calcium hypochlorite (NaOCl, $Ca(OCl)_2$) have been used as chlorine sources (Ahmadiantehrani *et al.*, 1991; Scheiner, 1987; Afenya, 1991).

These compounds all act in the same basic way. The following redox reactions show the fundamentals of this process (Ahmadiantehrani *et al.*, 1991; Scheiner, 1987):

$$Cl_2 + 2OH^- = OCl^- + Cl^- + H_2O \quad (3)$$

The cathodic reaction is

$$OCl^- + H_2O + 2e = Cl^- + 2OH^- \quad (4)$$

The anodic reaction is

$$2OH^- = \tfrac{1}{2}O_2 + H_2O + 2e \quad (5)$$

Eventually, the hypochlorite and the oxygen that is generated reacts with the carbonaceous material, resulting in passivation or de-activation of the carbonaceous material (Ahmadiantehrani *et al.*, 1991; Scheiner, 1987; Afenya, 1991). Working with a carbonaceous Carlin ore using gaseous chlorine at a pH value of 5 and Cl_2 addition of 450 kg/t, Sibrell (1991) found from the infrared (IR) spectra that carbonyl structures were formed during the treatment of the carbonaceous material. Passivation of the carbonaceous matter was comparable to autoclave passivation with high oxygen pressure, because of the strong oxidizing conditions used. Similar treatment using sodium hypochlorite passivated the carbon to a lesser extent than that obtained with gaseous chlorine. In general, the carbon content did not seem to change during the treatments, showing that the carbon was not destroyed. However, after strong oxidation with gaseous chlorine, it seemed that some of the carbonaceous material was oxidized to humic acid as evidenced from infrared analysis. The surfaces of carbonaceous matter are modified by chlorine, either by the formation of a chlorohydrocarbon layer or by the formation of carbonyl structures, composed mainly of carboxyl groups (–COOH). These surface groups passivate the carbon by blocking active adsorption sites. It has been suggested that ionization of surface charge in alkaline solution results in a negative charge at the surface of the carbonaceous material, thus repelling the negatively charged gold-cyanide ions and decreasing gold adsorption (Sibrell *et al.*, 1990).

Additionally, these chlorine compounds react with associated sulfides and dissolve most of the free gold (Ahmadiantehrani *et al.*, 1991; Scheiner, 1987; Afenya, 1991):

$$MS + 4OCl^- = M^{2+} + SO_4^{2-} + 4Cl^- \tag{6}$$

In the late 1980s, Newmont's Carlin Operation introduced a *flash* chlorination system (Brunk *et al.*, 1988) whereby chlorine was injected over a short time (~15 min) into small tanks, and then the concentration of hypochlorous species decayed through the oxidation circuit for about 1 h at 1 g/L hypochlorous acid, which is required for satisfactory carbon deactivation. In general, the chlorine consumption ranged from 30 to 50 kg/t ore depending on mineral constitution, especially the sulfide content.

At Jerritt Canyon in Nevada, milled alkaline slurry was treated by double oxidation, first with air at 70–80°C and 6–8 psig; the sulfuric acid produced was neutralized with lime, and then the second oxidation with chlorine took place. The retention time was about 20 h. The residual chlorine/hypochlorite was destroyed and the slurry went to a standard CIL circuit (Birak and Deter, 1987; Anonymous, 1996; Afenya, 1991). The double oxidation at Jerritt Canyon produced gold recoveries of 90–93% (Simmons, 1996). In another study, chlorine consumption of 36–90 kg/t was reported (Scheiner, 1987). Chlorination is particularly unsuitable for carbonaceous ores with sulfide content exceeding 0.5–1%, because of the excessive chlorine consumption (Anonymous, 1996).

These plants are no longer in operation. Newmont's chlorination plant was gradually discontinued in early 1990s, due to a lack of carbonaceous oxide ore. The increasing sulfide content in the ore also resulted in high chlorine consumption. In addition, the chlorine price increased dramatically in the 1990s. Both changes in ore type and chlorine price caused the chlorination process to become uneconomic.

3.5. Pressure oxidation

This technique uses autoclave leaching with pure air/oxygen, high pressure and temperature for the treatment of refractory carbonaceous ores treatment (Sibrell, 1991; Schmitz *et al.*, 2001b). Pressure oxidation is used to treat highly refractory sulfide ores containing chalcopyrite, pyrite, pyrrhotite, and/or arsenopyrite to release gold for subsequent cyanidation; this is discussed in detail in Chapter 15.

As tested by Sibrell (1991; Sibrell *et al.*, 1990), some autoclaved natural carbon samples seemed to develop new functionalities, specifically carbonyl structures, based on IR analysis. Other autoclaved samples did not show any change in the IR spectra. However, all the samples after treatment with oxygen under pressure showed a significant decrease in preg-robbing. *K* values decreased from 290 mg Au/kg CM to 1.5 mg Au/kg CM after autoclave treatment. There was not a significant decrease in the carbon content, which indicates that the carbon need not be destroyed. These results are similar to the results obtained by chlorination (Sibrell, 1991). In both cases, preg-robbing is minimized by passivation of the carbonaceous material.

Carbonaceous gold ores with low carbonate content from Twin Creeks was treated by pressure oxidation at a pilot-plant scale. These tests showed a reduction in gold recovery by cyanidation due to gold solubilization by chlorine from the processing water and precipitation on the carbonaceous matter, even at low chlorine concentrations (15–20 mg Cl^-/L) (Simmons *et al.*, 1998). The most important parameter seems to be the acid concentration in the autoclave. Addition of limestone, dolomite or proper ore blending overcame the problem. Also, operating the autoclave to lower temperatures (~200°C) resulted in an increase in gold recovery (Simmons *et al.*, 1998).

3.6. Nitric acid treatment

The Nitrox and Arseno (Redox) processes have been developed to treat sulfide refractory gold ores; however, they may be used for carbonaceous ores since the oxidation with nitric acid has been shown to passivate to some extent the carbonaceous material and reduce gold adsorption (Anonymous, 1996; Afenya, 1991; Díaz and Snihvrowych, 2004). The reaction kinetics for this treatment are fast, but they are considered to be chemically complex processes (Anonymous, 1996). Additionally, these processes release nitrate compounds, which are subject to stringent environmental control.

Moreno-Castilla *et al.* (1995) working on activated carbons with different degrees of activation showed that the treatment with nitric acid decreases the surface area and the microporosity within the carbons. Effects on carbons with higher degrees of activation are more dramatic. They found the presence of carboxylic groups and probably carboxylic-carbonate structures, as well as nitro and nitrate groups. One important finding in this research was determination of oxygen fixed on the carbon due to the nitric acid treatment Moreno-Castilla *et al.*, 1995). A recent study of nitric acid treatment of activated carbon using X-ray photoelectron spectroscopy (XPS) and FTIR analyses detected oxygen surface groups with single C–O bond, lactone, quinone or conjugated ketone, besides the carboxyl and carboxyl-carbonate groups detected before (Moreno-Castilla *et al.*, 2000). Since *active* carbonaceous matter in gold-bearing ores appears to be chemically equivalent to activated carbon, it is expected that the decrease in gold adsorption observed for nitric acid-treated activated carbon will also occur in the case of carbonaceous matter under nitric-acid treatment. Ongoing research at the University of Utah has shown that nitric-acid treatment of activated carbons results in reduction in gold adsorption from 87% to 22% and even to 2%

after 1 h of adsorption and a reduction in *K* value from 22 kg Au/t carbon to 0.9 kg Au/t carbon (Díaz and Snihvrowych, 2004).

3.7. Microbial deactivation

At present, there are at least three patents related to microbial treatment of sulfidic-carbonaceous gold ores. Hutchins *et al.* (1988) patented a process using thermophilic bacteria, like *Sulfolobus* and facultative-thermophilic bacteria, which will oxidize the sulfide minerals of the ore. The bioleached material is then treated using a blinding agent to inhibit the preg-robbing by the carbonaceous matter. Gold is finally recovered from the ore using cyanide or thiourea (Brierley and Wan, 1990).

Portier (1991) in his patent proposed to use heterotrophic microorganisms, which would be able to consume carbon. The residual ore is expected to be colonized by autotrophic microorganisms or to be treated by conventional hydrometallurgical processes.

According to Brierley and Kulpa (1992), gold-bearing ore is subjected to a bioleaching process to oxidize the sulfide minerals and liberate the gold. The ore is then inoculated with a bacterial consortium in the presence of a specific nutrient medium for the culture. This particular bacterial consortium deactivates the carbonaceous material that causes preg-robbing. It seems that the bacterial consortium acts as a biological blinding agent. After biological treatment the residual ore is then leached with an appropriate lixiviant to dissolve precious metals for the ore (Kulpa and Brierley, 1993; Brierley and Wan, 1990).

3.8. Thiosulfate leaching

Ammoniacal thiosulfate leaching has been tested for a variety of complex ores where cyanide does not work effectively, both at the laboratory scale and in a heap-leaching pilot-plant (Li *et al.*, 1995; Wan and LeVier, 2003). Several studies have been carried out on carbonaceous ores (Abruzzese *et al.*, 1995; Hemmati *et al.*, 1989; Wan and Brierly, 1997; Schmitz *et al.*, 2001a; Wan and LeVier, 2003). They showed, in general, good performance with relatively high recoveries, dependent on the ore characteristics.

One of the most important features of the thiosulfate process is the fact that activated carbon has a very low affinity for the gold-thiosulfate complex, which accounts for the effectiveness of the process in the treatment of carbonaceous ores (Gallagher *et al.*, 1989, 1990). For example, two leach-residue samples of low-grade carbonaceous ore from Gold Quarry (Carlin) were studied to establish the deportment of the unleached gold (Chryssoulis and Wan, 1997). After bio-oxidation pre-treatment, one sample underwent chlorination followed by CIL, while the second sample was subjected directly to an ammonium thiosulfate leach. The results showed gold in the CIL residue since the chlorination process did not completely passivate the carbonaceous matter, resulting in some gold preg-robbing after cyanidation. In the thiosulfate residue, on the other hand, preg-robbed gold was not significant. The thiosulfate leach process did not suffer from preg-robbing effects.

The reasons for the very low loading of gold onto carbon in the thiosulfate system have not been fully elucidated at this point, but various possibilities exist, including the relatively high negative charge of the complex, steric limitations/polarity due to molecular structure, and the lack of specific interactions of the ligand group with active carbon sites (Wan *et al.*, 1993).

Wan *et al.* (1994) patented a process for treatment of sulfidic-carbonaceous ores by copper-catalysed ammonium-thiosulfate leaching after a bio-oxidation process. They tested this procedure in a pilot-heap leach using bio-oxidized material. Gold recoveries from heap leaching as high as 70% were obtained, whereas the conventional cyanidation process resulted in recoveries of only 20%. Gold was recovered from thiosulfate solution by cementation with copper and the ammonium-thiosulfate solution was recycled to the heap. Based on laboratory and pilot-plant test results, the bio/thio process was developed and carried out for several years to treat carbonaceous sulfidic ores as revealed from the data presented in Table 3. A similar process was also developed by Pappas (1997) for treating carbonaceous oxide ores.

A recent study on Goldstrike ore (Schmitz *et al.*, 2001a) reports gold recoveries from 90% to 100% using copper-catalysed ammonium thiosulfate leaching on autoclaved carbonaceous ores, since about 60% of the gold was encapsulated in sulfides. They demonstrated that thiosulfate dissolved all the gold that used to be preg-robbed by the carbonaceous material during cyanidation.

Schmitz (2000) and Schmitz *et al.* (2001a), working with mini-column beds of carbonaceous material, suggested a kinetic limitation due to the slow

Table 3
Thiosulfate heap demonstration plant at Newmont, Nevada operation (after Wan and LeVier, 2003)

Campaign year	Leach type	Tonnes	Gold produced	
			(oz)	(kg)
1996	Bio/thio	326,500	11,850	368.5
1997–1998	Direct thio	324,000	20,100	625.1
1998	Bio/thio	331,100	11,370	353.6
1998–1999	Direct thio	259,800	12,470	387.8
Total CSR ore treatment		1,241,400	55,790	1735.0

re-oxidation reaction of cuprous ion as shown in the following reaction as studied by Li *et al.* (1995):

$$Au^0 + 5S_2O_3^{2-} + Cu(NH_3)_4^{2-} = Au(S_2O_3^{3-} + Cu(S_2O_3)_3^{5-} + 4NH_3 \tag{7}$$

Copper oxidation by O_2 or another oxidant

Also, Li *et al.* (1996) found that an appropriate ammonia-thiosulfate concentration ratio must be maintained to sustain the continual cuprous–cupric redox reaction, without stabilization of copper. This was also confirmed in a pilot-plant scale study (Wan and LeVier, 2003).

The leaching of gold with ammoniacal thiosulfate is the subject of Chapter 22.

4. NON-CARBONACEOUS PREG-ROBBING

Gangue minerals as well as sulfides have been suggested to have gold preg-robbing characteristics. Preg-robbing mechanisms may be gold reduction, physical adsorption or chemical adsorption (Rees and van Deventer, 2000; Tan *et al.*, 2003; van Vuuren *et al.*, 2000a,b; Adams *et al.*, 1996).

Adams *et al.* (1996) demonstrated preg-robbing effects in various copper minerals, clays and high surface-area river sands, with various mechanisms attributed to the different minerals.

van Vuuren *et al.* (2000b), working on shale material from Beatrix Gold Mine in South Africa, found that phyllosilicates such as pyrophyllite, muscovite and chlorite are decomposed in strong alkaline solutions, causing a drop in the pH. At these conditions, it seems that gold co-precipitated with colloidal $Mg(OH)_2$ and $Fe(OH)_3$ on the ore surface. This study suggested that pyrophyllite and muscovite may be important factors in the adsorption of gold from solutions on the solid surface of the ore particles.

On the other hand, among sulfide minerals, chalcopyrite was found to be strongly preg-robbing, while pyrrhotite and pyrite have been shown to adsorb gold to a lesser extent. Rees and van Deventer (2000) found that in a cyanide-deficient system, chalcopyrite adsorbs the gold almost immediately from solution, while pyrite adsorbed about half the gold. However, it was evident in this study that not only the deficit of cyanide was responsible for preg-robbing, but the presence of reactive sites on the sulfide surfaces. Using topological studies by scanning-electron microscopy/energy-dispersive X-ray analysis (SEM/EDX), Tan *et al.* (2003) and Feng and van Deventer (2001) showed that gold was adsorbed at defect edges on the chalcopyrite and pyrite grains. Using a carbon-coating chalcopyrite sample, they found that gold was not only adsorbed at the defects sites but also at the smooth surfaces. By XPS studies, Tan *et al.* (2003) established that gold adsorbed on chalcopyrite was mostly reduced to metallic form. The presence of carbonaceous material enhanced the gold adsorption by sulfides minerals.

The overall mechanism suggested by Rees and van Deventer (2000) for the reduction of aurocyanide at a chalcopyrite surface can be expressed as

$$4\mathrm{Au(CN)}_2^- + \mathrm{CuFeS}_2 + 2\mathrm{OH}^- = 4\mathrm{Au}^0 + \mathrm{Fe(OH)}_2 + \mathrm{Cu}^{2+} + 2\mathrm{S}^0 + 8\mathrm{CN}^- \quad (8)$$

A similar analysis was used by Quach *et al.* (1993) to explain the mechanism of gold reduction by pyrrhotite.

The study of Tan *et al.* (2003) also showed that preg-robbing of chalcopyrite increased with a decrease of pH, to a minimum at pH 11. However, at higher pH values (11–12.5), adsorption was found to increase. The gold adsorption by chalcopyrite was reversible, depending on cyanide concentration. Carbon-coated chalcopyrite maintained the strong preg-robbing behaviour at higher cyanide concentrations.

Feng and van Deventer (2001) found that in thiosulfate-deficient solutions, chalcopyrite, pyrite, arsenopyrite, kaolin and quartz showed preg-robbing characteristics. However, preg-robbing in the thiosulfate system was enormously reduced compared to the cyanide system even with a low free thiosulfate concentration.

5. EXAMPLES OF PLANT PRACTICE

The design of industrial operations for gold recovery depends on the mineralogical complexity of the ore, which determines the metallurgical alternatives for efficient processing. As mentioned before, not all carbonaceous materials are preg-robbers, and also, the severity of the preg-robbing depends mainly on the maturity of the carbon. In addition to natural carbon, the ore can contain sulfides and/or oxides, and gangue. All the components have to be taken into account during the evaluation of process alternatives.

The oxidation methods have been found to be the most effective for removal of carbonaceous material and oxidation of sulfides (Sibrell, 1991; Anonymous, 1996; Fernández *et al.*, 2000; Guay and Peterson, 1973; Afenya, 1991). However, these processes are expensive, so an agreement between costs and gold recoveries must be achieved.

Some examples of actual technologies used for refractory sulfidic carbonaceous gold ores are discussed below.

The complexity of the Carlin trend ores has caused Newmont, operator of major mines in this deposit, to develop and use several combination processes, like inert gas flotation ($\mathrm{N_2}$-TEC®), bio-oxidation heap-leach technology (BIOPRO®), pressure-oxidation (POX) technology, roasting and ammonium-thiosulfate heap-leaching as recovery treatments for refractory sulfidic-carbonaceous ores.

Refractory ore has recently accounted for 66% of the total ore processed by the Newmont operations in Nevada, 52% being treated by Twin Creeks autoclaves, 16% by Lone Tree autoclaves and 32% by the Carlin roaster. Newmont probably possesses the widest variety of processing methods of any gold district in the world. Fourteen active processing facilities, ranging from autoclaves and a roaster to flotation cells and cyanide and thiosulfate heap-leaching, allow Newmont to maximize the economic recovery of gold from a wide variety of ore types and grades. It has been reported that gold recovery from these refractory ores ranges from 85% to 90%.

Macraes Gold Project, New Zealand, nowadays is using the Newmont POX technology to treat refractory sulfidic carbonaceous ore, achieving gold recoveries of 84%, higher than the historical 70–75% recovery, according to Cadzow and Giraudo (2000). Macraes is the first plant using POX on gold flotation concentrates. Concentrate feedrate to the autoclave is 23.3 t/h, with a concentrate particle size of 18 μm. Operating conditions are 225°C and 3,140 kPa.

According to Rees and van Deventer (2000), the Stawell Gold Mine, Australia, inhibited the preg-robbing by blinding the carbonaceous ore with diesel or kerosene at a concentration of 200 mg/L. Since kerosene also acts on the activated carbon used in the leaching circuit, addition of kerosene can be suspended every few weeks to restore the activity of the activated carbon. This is possible as Stawell has several ore types, some of which are non-preg-robbing. By careful ore characterization, a preg-robbing ore is treated for several weeks, with kerosene addition, followed by a campaign of non-preg-robbing ore (without kerosene addition) while the carbon is reactivated.

Barrick Goldstrike Mine is treating the refractory sulfidic carbonaceous ore in a “state-of-art” roaster, which is the largest in the world able to treat ore at 16,450 t/d, according to Barrick’s web page. The roaster was completed in 2000. Goldstrike also operates six autoclaves for sulfide oxidation.

Placer Dome’s Cortez Mine has processed 7.8 Mt of carbonaceous ore in 5 years. In 2003, the revenue for the carbonaceous ore sold to Barrick represented 8% of the total gold production. From 1990 to 1996, Cortez treated the refractory sulfidic carbonaceous ore in a fluid bed roaster at their own plant. Since 2001, Placer Dome has sold the Cortez carbonaceous ore mainly to Barrick and eventually to Jerritt Canyon in 2001. New research and engineering projects have resulted in two new processes viable for the carbonaceous ore, the thiosulfate leaching and a cyanide-based process using resin (Handley, 2002).

On the other hand, Placer Dome’s Turquoise Ridge, in a joint venture with Newmont, treats 1,800 t/d of refractory sulfidic carbonaceous ore in the Twin

Creeks Sage Mill, using pressure oxidation followed by CIL, carbon elution, zinc precipitation and refining.

Kumtor in Kyrgyzstan, central Asia, treats 15,000 t/d by flotation, followed by CIL processing of the concentrate and tailings in parallel circuits, carbon elution, electrowinning and refining. Gold recoveries are about 76–80% depending on the carbon content of the ore (Kergoat and Shaildaeva, 2000).

The Penjom Gold mine in Malaysia is considered to be the first gold-processing plant in Southeast Asia successfully utilize RIL technology to treat primary gold-bearing carbonaceous ores. In 1999, the RIL process replaced the CIL circuit. Gold recoveries are currently around 90% (Avocet Mining, 2004).

6. PRACTICAL ORE CHARACTERIZATION

Newmont and other gold-mining companies have used a preg-robbing analytical method to quantify the preg-robbing characteristics of refractory gold ores. The analytical method includes (1) analysis of cyanide-leachable gold of a specific ore sample and (2) spiking a certain amount of gold cyanide into a cyanide leach of the sample (in general, 3.4 mg/L of gold as gold cyanide is added), followed by analysis of gold in solution after cyanide leaching (Wan, 1996). The loss of gold in the final cyanide solution depends on the content of preg-robbing materials in the ore sample and their activity. Thus, the preg-robbing value (or activity) of the sample can be characterized as:

$$\text{Preg-robbing value} = \text{AuCN (ppm)} + 3.4\ \text{ppm} - \text{AuPR} \tag{9}$$

where AuCN is the cyanide-leachable gold of an ore sample, AuPR is the final gold concentration after being preg-robbed and 3.4 ppm is the amount of gold spiked into the leach experiment (Wan *et al.*, 1994).

For a high preg-robbing carbonaceous ore sample, the AuPR approaches to zero (gold is totally adsorbed or preg-robbed), therefore, the preg-robbing value would be > 3.4 ppm. For a non-preg-robbing ore sample, AuPR is equal to the concentration of AuCN plus the spiked 3.4 ppm gold, which yields zero preg-robbing value. This preg-robbing index helps geologists, mining engineers and metallurgists in the gold industry to characterize a preg-robbing ore deposit (Wan *et al.*, 1994).

Newmont Mining Corporation Technical Facility has established the following laboratory test-procedures for characterizing gold deportment for refractory sulfidic-carbonaceous ores (Wan, 1996; Wan *et al.*, 1994). The test procedures are selected based on mineral characteristics of the refractory ore sample. In general, the test procedures include pre-oxidation treatment or acid leaching followed by cyanide leaching. Mineralogical analysis of feed sample and leach residues are required.

The test procedures include:

- direct cyanide leach to identify free-milling gold in the ore sample;
- NaCN-CIL with a variable amount of activated carbon addition (20–40 g/L carbon) to characterize preg-robbing activity;
- low-temperature nitric acid treatment followed by NaCN leach and/or NaCN-CIL to identify the amount of gold associated with or locked in easily oxidized sulfide minerals such as arsenopyrite and secondary copper minerals;
- elevated temperature nitric acid treatment followed by cyanide leach and/or NaCN-CIL to examine the amount of gold associated with or locked in sulfide minerals including pyrite; and
- direct hydrochloric acid leaching followed by cyanide leach and/or NaCN-CIL to examine the amount of gold associated with iron oxides and other acid-soluble minerals.

The amount of non-cyanide-leachable gold remaining in the leach residue after acid treatment is mostly related to preg-robbing, which should be compared with direct cyanide leach and NaCN-CIL results. Alternatively, a thiosulfate leach is preferred instead of cyanide leach for highly preg-robbing ore.

It is extremely important to examine the mineralogy characterization after each test and compare with the feed sample.

Barrick Goldstrike Mines (BGMI) uses two standard tests to assess the preg-robbing behaviour of gold ores.

The preg-robbing test (%PR) is a simple test using 10 mL of a 2 g/L NaCN solution with 3 ppm gold to 5 g of ore. After equilibrating for 1 min, the slurry is centrifuged and the supernatant is analysed for gold concentration in solution (in ppm). The %PR is determined as (Schmitz *et al.*, 2001a)

$$\%\mathrm{PR} = \left(1 - \frac{3 - [\mathrm{Au}]}{3}\right) \times 100 \tag{10}$$

where [Au] is the gold concentration in the supernatant solution.

The second test (%REC) involves bench-top autoclaving followed by a CIL process (BTAC-CIL), to measure the gold recovered by commercial activated carbon (AC). A 1:1 solid/liquid ratio (200 g, 90% by weight less than 150 mesh in size/200 g water) is acidified with sulfuric acid to dissolve any carbonates. The acidified slurry is blended for 15 min and then diluted with water to around 500 g total weight, and autoclaved for 1 h at 240°C with O_2 overpressure at 420–880 kPa. A NaCN concentration of 2.3 kg/t slurry with 12 g/L slurry of AC is used and allowed to equilibrate for 16 h in a bottle-roll test. Once separated by screening, the AC is analysed for gold by fire assay. The ratio between the gold content in the AC and the gold content in the untreated ore gives the %REC (Stenebråten *et al.*, 2000; Schmitz *et al.*, 2001a):

$$\%\mathrm{REC} = \frac{[\mathrm{Au}]_{\mathrm{AC}}}{[\mathrm{Au}]_{\mathrm{ore}}} \times 100 \tag{11}$$

These two Barrick tests differ in many aspects. The %PR test measures the aurocyanide complex loss from a spiked solution by the preg-robbed ore. The %REC test includes additional ore treatments related with industrial ore-processing in some of Barrick's operations, and shows the effectiveness of these procedures to deal with different ore types like sulfide and carbonaceous preg-robbing ores (Stenebråten *et al.*, 2000; Schmitz *et al.*, 2001a, b). An inverse relationship between %PR and %REC is expected (Schmitz *et al.*, 2001a).

Even though standard blinding tests have not been established, some procedures can be mentioned.

Blinding laboratory tests carried out by Newmont Metallurgical Services, use different inorganic and organic chemical compounds as blinding reagents. A small-scale laboratory CIL test consists of 20 g of ore agitated with 80 mL solution containing 0.2 g of the blinding reagent for 2 h. After this pretreatment, the pH value is adjusted to 11–11.5 with NaOH. Sodium cyanide (0.15 g) and activated carbon (3 g) is added and the pulp agitated for 24 h. AC is screened out, the solution is filtered and AC and ore residue are dried. Gold concentration in the ore residue and AC are determined by fire assay. Gold extraction by AC is determined. A larger laboratory CIL test consists of 100 g, 80% by weight less than 200 mesh in size of ore, 20 g/L AC, 10 g reagent/kg ore in a 1:4 (w/w) S/L relationship (Newmont Metallurgical Services, 1989).

Matsuev *et al.* (1968) suggested a procedure using 1:1 S/L with 150 g of ore concentrate in water using 200 g/t of blinding reagent. Pulp is diluted to a S/L ratio 1:2. Sodium cyanide concentration of 0.13% is added as well as CaO. Peroxide is also added as a source of oxygen (BaO_2). The pulp is stirred for 12 h then filtered. The solution is recovered and analysed for gold.

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Chapter 39

Treatment of gold-telluride ores

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1. INTRODUCTION

Gold tellurides have been treated commercially in only in a small number of regions in the world – most notably in Kalgoorlie, Western Australia; Vatukoula, Fiji; Cripple Creek, Colorado and Kirkland Lake, Ontario.

The leaching of telluride ores has always been problematical with a perceived mismatch of findings between researchers and operators as to the recoverability of gold by cyanide leaching of gold-telluride ores without some form of oxidative pre-treatment step.

The question as to whether cyanide can successfully recover gold from gold-telluride ores has long been debated. W.E. Johnston in his 1933 paper entitled "Tellurides – Problem or Alibi?" recorded that "many writers have reiterated the statement that tellurides are responsible for the metallurgical troubles associated with these ores". He noted that laboratory testwork results on such ores was sometimes "obscure and unexplainable" but if the ores were finely ground, the phenomenon was not often observed.

1.1. Tellurium-bearing ores and materials

The simplest and most common association of tellurium with gold is as the mineral calaverite [$AuTe_2$], but other metal associations also occur. Silver associations give rise to the minerals petzite [Ag_3AuTe_2], sylvanite [$(Au,Ag)Te_2$] and krennerite [$(Au,Ag)Te_2$]. A gold-telluride association with antimony also occurs with the mineral montbrayite [$(AuSb)_2Te_3$], while kostovite [$CuAuTe_4$] has a copper–gold–tellurium association.

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Many non-gold-associated telluride minerals also occur, most notably coloradoite [HgTe], altaite [PbTe] and hessite [Ag_2Te].

Tellurium is occasionally found uncombined in nature but is mostly produced as a by-product of the electrolytic refining of blister copper. It is used as an additive to steel and is often alloyed with aluminium, copper, lead, or tin. It is used in vulcanizing rubber, as a colouring agent in glass and ceramics, and in catalysts for petroleum cracking. It is a semi-conductor material and is slightly photosensitive. Its price is a function of its purity – the high-purity metal currently sells for around US$2/g, whereas commercial-grade tellurium retails for around US$30/kg. The world market for the metal is modest, with total estimated world production in 1998 of only 250 tonnes.

Calaverite [$AuTe_2$] is the most common of the gold-bearing telluride minerals. It was first discovered in 1861 and takes its name from Calaveras County in California where it was first found.

Its physical characteristics are given in Table 1.

When heated in air to around 500°C the gold tellurium bond is readily broken, producing tellurium dioxide and gold metal. Above 800°C the TeO_2 sublimes off.

The mineral itself is remarkably gold rich with the gold being found in a molecular association with the element tellurium. On a weight basis some 44% of the weight of the mineral is gold.

1.2. Toxicity

Metallic tellurium and tellurium compounds should be considered toxic and need to be handled with care. Humans exposed to as little tellurium as 0.01 mg/m^3 in air can develop *tellurium breath*, which has a garlic-like odour.

1.3. Assaying

Telluride ores present unique challenges to the fire assayer. Tellurium can cause low values for both silver and gold during the cupellation process by reducing the surface tension of the precious metal prill, leading to losses into the cupel. It is thus important to ensure removal of the tellurium during the

Table 1
Physical properties of calaverite

Colour	Silver white to brassy yellow
Lustre	Metallic
Specific gravity	9.1–9.3
Hardness	2.5–3.0
Melting point	464°C
Fracture	Brittle – conchoidal
Gold content	43.6%

fire assay fusion. This is accomplished by ensuring that the fusion is carried out under strong oxidizing conditions so that the tellurium reports to the slag rather than to the lead phase. Should a sample not be initially identified as containing tellurium, a telltale *colour de rosa* residue is left on the cupel. If this is seen to occur, the sample should be reassayed with a different flux mixture.

It is generally helpful to reduce the sample weight for such ores in order to increase the flux/sample ratio. This increases the likelihood of a successful fusion resulting in a clean two-phase separation.

2. HISTORICAL TREATMENT METHODS

Gold-telluride ores were not immediately recognized for their gold-bearing capacity. Visually, these ores did not contain the same dull brassy yellow typical of free gold. It was with some surprise that the returns from treatment plants greatly exceeded the miners expectations. The identification of tellurides as a significant source of gold quickly led to miners identifying the mineral in its own right. A simple miner's test for gold tellurides consisted of spreading the mineral a few particles deep on a glass slide and heating it in a flame. The telluride fused, leaving a characteristic island of telltale gold surrounded by a pool of tellurium oxide.

Gold-bearing tellurides are silvery to pyrite-yellow, commonly striated, unlike gold, which is a deeper yellow and rarely crystalline.

Some mineral indicators of gold tellurides were observed that assisted in its detection. A distinctive green ore (green leader), taking its colour from a vanadium-bearing mica, has sometimes accompanied telluride gold.

2.1. Cripple Creek

The first modern treatment of gold-telluride ores was carried out in the Cripple Creek goldfield in the Rocky Mountains in Colorado, USA. Discovered in 1891, it was then one of the richest goldfields in the world. As the deposits at Cripple Creek were close to the surface, little capital was required to start a mine, and most were initially owned and operated by groups of prospectors.

The relatively high specific gravity of the mineral (9.2) allowed it to be concentrated by gravity techniques such as blanketing tables, which retained the heavier weight particles. The introduction of the Wilfley table in 1903 further improved gold recovery by utilizing longitudinal riffles that caught gold and mineral particles from material flowing diagonally across the table. The gravity concentrates so produced were smelted to yield the gold metal.

Such techniques, while being suited to coarse particles, were inefficient in capturing the fine particles, resulting in significant gold losses. The problem was further compounded by the brittleness of the mineral, which when crushed or milled tended towards the finer particle sizes. To assist in overcoming these losses, chemical methods were quickly devised to extract gold from the mineral. Chlorination proved to be a successful lixiviant and quickly became popular as a treatment method, with most of the large independent mills around Cripple Creek mills using chlorine by 1898. The establishment of such plants pre-dated the use of the cyanide process, which was patented by John Steward MacArthur in 1887. Cyanide quickly proved to give superior gold recoveries to those achieved using chlorine, but its introduction was resisted in many locations due to the high royalty payments that were demanded, and by the capital investment already made in the older-style treatment plants. However, by 1907, the use of roasting to oxidize the ore prior to cyanidation of the calcine was firmly established as a major method of treatment of Cripple Creek ore. By the use of a roasting step, the tellurium was burnt off as a gas, leaving behind the gold, which was then amenable to dissolution with cyanide. Roasting had the inherent advantage that gold in almost any type of refractory ore could be recovered after this process. It thus became popular around the world due to relatively low cost and excellent gold recovery rates. Both whole ore roasting (a dry process) and roasting of only a concentrated portion of the valuable component were practiced (see Chapters 17 and 18).

2.2. Kalgoorlie

The second major goldfield where tellurides became an important source of gold was in Kalgoorlie, Western Australia, where gold was first discovered in 1893. The presence of tellurides were soon recognized based upon the experience of Cripple Creek miners, with specimen-quality telluride material being sent for exhibition in the 1900 Paris World Exposition. As reserves of oxidized ore were running out, very rich pockets of sulfo-telluride ores were discovered within the main lodes of several mines.

Concentrating and smelting techniques were found to be able to successfully recover most of the telluride-associated gold, achieving around 95% recovery without a leach step; however, because no smelting facility was available locally, the ore had to be transported to suitable smelters in the eastern colonies (South Australia and New South Wales). The smelters operated as copper or silver-lead smelters but were adapted to deal with shipments of gold ore. Eventually, in 1903, a local smelter was built on the coast at Fremantle, approximately 600 km from Kalgoorlie.

Some of the sulfo-telluride ores mined between 1897 and 1900 were very rich indeed, grading around 500 g/t. Concentrating devices were employed to reduce the mass of ore that had to be transported; however, such concentration was inefficient and when higher-grade ore was treated, the overall extraction was poor.

The presence of up to 15% calcium and magnesium carbonate in the Kalgoorlie ore ruled out any possibility of using chlorination in place of smelting due to the very large chlorine consumption of these ores.

Cyanide was introduced to leach the product of whole-ore roasting – a dry grinding process. Extractions were good, but costs were high because of the dry grinding and fuel required to roast an ore of relatively low sulfide content.

Attempts to use direct cyanidation of the concentrates produced from a concentration step proved to be largely unsuccessful, with the preferred method being to roast the concentrate. However, many roasters of the time suffered from significant dust losses with inefficient dust capture resulting in the loss to atmosphere of high-grade gold material. This, and the need to leach the unsatisfactorily high-grade gold of the concentration tailings, spurred the development of an efficient leaching process that did not require the pre-treatment step of roasting.

As early as 1894, research in Britain had shown that the addition of bromocyanide to the normal cyanidation process improved its efficiency with certain problematic ores including tellurides. A company was formed to exploit the patent for the process (the Sulman Teed process) and was based in the Kalgoorlie goldfields. The process was refined by the company's chief chemist, Dr L. Diehl. The Diehl process, as it became known, was able to treat telluride ores by incorporating the use of bromocyanide from the Sulman Teed process, along with a new innovation, the tube mill. The tube mill allowed for the efficient fine grinding after the amalgamation and the removal of concentrates. It had become clear that fine crushing was essential for bromocyanide to be effective on the sulfo-telluride ores. The reagent is a volatile crystalline solid, soluble in water, and when mixed with alkaline cyanide, forms a very powerful and rapid solvent for gold (see also Chapter 21). In the presence of excess alkali, the compound is rapidly broken down to bromide and cyanate and therefore must be used in solutions containing little or no free cyanide.

The tube mill (the forerunner to the ball mill) consisted of a revolving steel cylinder supported on rollers at a slight angle to the horizontal so that the pulp moved continuously through the mill. The fine crushing was performed by the use of very hard Norwegian flints, which took up about half of the mill volume. The first commercial Diehl plant was commissioned in Kalgoorlie in March 1900.

2.3. Kirkland Lake

Gold-telluride ore from the Wright-Hargreaves Mine at Kirkland Lake, Ontario, were also treated using bromocyanide. J.T. Willey in 1925 described the treatment of a flotation concentrate by bromocyanide as extracting 98% of the gold values. By the 1930s, the Wright-Hargreaves mill practised an initial cyanidation step for non-refractory gold followed by filtration, flotation of the residual tellurides, and fine grinding of the concentrate in a pebble mill with a high lime addition (12 kg/t of concentrate). The finely ground concentrate was then cyanide-leached for a prolonged time period and the leached pulp returned to the primary leach circuit. Overall plant recovery was in excess of 96%.

Other plants in the Kirkland Lake area, for example Lake Shore Mines, used cyanide leaching of the ore to recover non-refractory gold, and floated a sulfide-telluride concentrate which was then roasted.

2.4. Fiji

Gold and gold tellurides are also widely distributed in the Fijian Islands. In 1932, B. Borthwick and J. Sinclair discovered payable gold on Vunisina Creek. Further investigation of this prospect, associated with the Tertiary Vatukoula volcanic caldera, led to the development of a number of mines, of which the famous Emperor mine has been in continuous production since about 1935.

Treatment of telluride ore began in Vanuwtu, Fiji, in 1934 using a conventional refractory treatment circuit employing roasting followed by cyanide leach of the calcine. A hydrometallurgical treatment method for the leaching of gold telluride along with the production of tellurium metal was devised at Emperor Gold Mine (Cornwall and Hisshion, 1976). The process (called the Emperor Process) used a basic hypochlorite (*i.e.*, chlorine) solution to oxidize a high-grade gold telluride concentrate produced from flotation. The flotation was carried out using lime and cyanide to depress sulfides giving a high-grade free gold, telluride concentrate. A number of other oxidation systems were found to be also successful, including $FeCl_3$ and MnO_2, but these were rejected because of difficulties encountered in the filtration step. A reagent combination of NaOH, Na_2CO_3 and $Ca(OCl)_2$ was used with the tellurium/chloride ratio controlled so as to achieve complete oxidation in 1 h. The solution was filtered with the solids portion then being subjected to cyanide leaching using 1.0–1.5% NaCN for 3–4 h. Adequate protective alkalinity is provided by the carryover reagents from the oxidation stage. The leach residue was filtered, reacted with Na_2S, and again filtered ahead of roasting.

The tellurium was precipitated from the chloride oxidation solution by the addition of Na_2S/Na_2SO_3. After filtration and washing the precipitate was dried and then smelted at 825°C to produce saleable ingots of the tellurium metal.

3. RECENT RESEARCH

3.1. Milling

The main gold telluride, calaverite [$AuTe_2$], being of a brittle nature, mills very readily. The common use of hydrocyclones to classify the mill product leads to a preferential overgrinding of this high-SG material over the other ore components. This results in a much finer average telluride mineral particle size than the host material. The fine particle size of the gold-bearing material has potentially undesirable side effects in downstream unit processes such as flotation, where the fine nature of the telluride minerals results in slow flotation kinetics and therefore some loss of gold to concentrator tails.

3.2. Flotation

A search of published literature has revealed a scarcity of information on the flotation of telluride minerals. This appears to be a reflection of the rarity of tellurides in gold deposits around the world.

From the time that flotation was introduced into the Kalgoorlie Goldfield – about the mid-1920s, it had been the aim of many metallurgists to produce a separate telluride concentrate from the bulk pyritic concentrate. They expected that by doing so, and treating each product separately, there would be improved gold recovery, reduced costs and perhaps the opportunity to recover tellurium as a by-product. It was not until 1961 that an actual plant test was carried out. Smith (1963) reported plant results similar to testwork results that showed excellent floatability of the Kalgoorlie telluride ores, to produce a high-grade telluride gold concentrate using copper sulfate and frother. The concentrate, after cleaning, graded 1270 g/t gold and 4.6% sulfur with only 0.55% mass.

Yan and Hariyasa (1996) also examined the flotation performance of a high-grade tellurium gold ore from the Kalgoorlie deposit. They showed that tellurides float readily at natural pH values (~8.0) with the addition of frother only, and that the recovery and rate of flotation could be improved by the addition of xanthates or mercaptobenzothiazol. The best selectivity between sulfides and tellurides was obtained between a pH value of 8.0 and 11.0. Individual telluride species were shown to have similar floatabilities, making them difficult to separate, with non-gold bearing tellurides such as altaite [PbTe] coloradoite [HgTe] also reporting to the flotation concentrate.

3.3. Cyanide leaching – testwork results

The cyanide leaching of tellurides has a history of controversy with some researchers maintaining that successful gold extraction could be achieved provided that certain conditions were met. Operationally, plant leaching proved to be not as successful as in the laboratory and certainly was not as robust as the leaching of free gold.

Henley *et al.* (1995) examined the technique of using high cyanide concentrations at high pH values to determine the gold telluride content of an ore. They took a high-grade +20 μm KCGM flotation concentrate and performed a two-stage leach. In the first stage, leaching was carried out using 0.1% NaCN at a pH value of 9.2 for 24 h. It had been suggested that the native gold would be dissolved under these conditions but not the telluride gold. A second stage using strong cyanide (2%) at pH 12.5 for 96 h was employed to dissolve the gold tellurides. They found that the first stage was a good estimator of the native gold content; however, the second stage failed to account for the gold associated with tellurides. Mineralogical studies showed that 6% of the telluride gold had been dissolved in the first stage and only 11% in the second stage.

The technique was further refined by Ellis (1998), who introduced an oxidative step using hypochlorite leaching before the second stage of cyanide leaching. For particles coarser than 10 μm, the oxidation and subsequent cyanidation was repeated a number of times to counter the observed effect that oxidation penetrated only a small distance into a mineral grain on each pass. When no further gold extraction was observed after oxidation, it was concluded that all the gold tellurides had been dissolved. Leach conditions were modified to a lesser cyanide concentration and lime used for pH control rather than caustic soda.

Jackman and Sarbutt (1990) found that solution changes during leaching gave a dramatic improvement in gold recovery on a 74 μm gold-tellurium concentrate grading 218 g/t Au, 410 g/t Te and 41.7% S, the major tellurium mineral being montbrayite [Au_2Te_3]. Gold recovery improved from 92% to 98% with two solution changes. The presence of carbon during the leach process (CIL) was shown to achieve a similar gold recovery. Lead nitrate was shown to be beneficial in reducing residue grades in all cases. Fine grinding of the concentrate to 22 μm with CIL leaching improved recovery further to 98.6%.

Pleysier *et al.* (2002) examined the leaching behaviour of gold tellurides from a KCGM flotation concentrate using both a laboratory and theoretical approach. Laboratory tests demonstrated conclusively that the concentration of tellurium in solution dropped after an initial increase in concentration. Carbon was shown to be effective in removing tellurium from solution. They concluded that the telluride-leach process was affected by the presence of sulfides, which were able to cause elemental tellurium to be precipitated from solution. Once precipitated, tellurium was unlikely to redissolved as this would involve breaking stable Te–Te bonds, whereas the oxidation of calaverite involves breakage of the weaker Au–Te bonds. It was postulated that such precipitates, if they occurred before the complete dissolution of the gold, could result in a passivating coating that severely limits the rate of gold dissolution.

3.4. Cyanide leaching – theoretical considerations

Gold tellurides have been shown to be readily oxidized under modest oxidizing conditions during cyanide leaching. The tellurium undergoes dissolution most likely as the tellurite ion (TeO_3^{2-}) and under more strongly oxidizing conditions as the tellurate ion (TeO_4^{2-}):

$$AuTe_2 + 4OH^- + 2O_2 \rightarrow Au + 2TeO_3^{2-} + 2H_2O \tag{1}$$

$$2TeO_3^{2-} + O_2 \rightarrow 2TeO_4^{2-} \tag{2}$$

Tellurium is involved in both oxidative reactions (Eq. (1)) and in reducing reactions (Eq. (2)). Should tellurium metal form, it would not easily re-oxidize into solution.

While sulfides *per se* are not necessarily a problem in precipitating tellurium, transitory sulfur compounds such as thiosulfate and *poly*sulfides provide a possible mechanism for the precipitation of elemental tellurium.

It is believed that the success of changes in solution conditions during the cyanide leach lies in the removal of some of the *poly*sulfides and also of the ionic tellurium species in solutions, thus reducing the amount of precipitated tellurium. Carbon is believed to act by providing a redox site for the preferential precipitation of tellurium. The use of lead salts is likely to be beneficial by assisting in the reduction of the *poly*sulfides, thus reducing the driving force of the reaction.

The use of high pH appears to be much more effective if lime is used rather than caustic soda. McMullen (2002) and Chryssoulis and Cabri (1990) have separately proposed that the benefit of lime lies not only in pH control, but more importantly in providing an excess of calcium ions. These ions are able to scavenge tellurium ions from solution in the production of a low-solubility precipitate, calcium hydrogen tellurite [$CaH_4(TeO_3)_3$]. By this means passivation of unleached gold by tellurium precipitation is reduced.

Work conducted at KCGM by Deschênes and Ellis (2002) showed that high levels of dissolved oxygen were not necessary for the successful leaching of KCGM concentrates that had been ground to around 12 μm. Dissolved oxygen (DO) levels as low as 1–2 ppm were shown to have a beneficial effect in reducing the cyanide consumption while maintaining gold recovery. Measured thiocyanate (SCN^-) levels in solution dropped from over 1,000 mg/L to under 200 mg/L, indicating that the cyanide side reaction with sulfur compounds had been significantly reduced. They showed that a continuing high DO demand was present throughout the leach and that the use of excess oxygen promoted the oxidation of the sulfide materials. The oxidation of the sulfides could be minimized by limiting DO, thus resulting in a much more cost-effective leach. They suggested that excess oxygen may have other detrimental effects such as passivating gold by coating it with insoluble sulfide oxidation products.

This finding conflicted with conventional leaching practice in that under normal circumstances a higher DO level promotes more rapid gold leaching kinetics, which often leads to a better gold recovery. To severely limit the DO and maintain or improve kinetics was counter-intuitive. Rumball and Houchin (2003) were able to provide a theoretical basis for this observation in conjunction with their own laboratory testwork. They suggested that the gold leach reaction for high-sulfide ores was under cyanide diffusion control rather than oxygen control as the sulfides themselves were able to act as a galvanic surface for the reduction of oxygen necessary for the leach reaction. As the cathodic area was increased (concentration of conducting sulfides) a lower dissolved-oxygen level was required to maintain the same rate of reaction. Thus, the typical cyanide ratios found necessary for the leach of oxide ores are not applicable to sulfide ores, particularly if finely ground with very high effective surface areas.

3.5. Other oxidative processes

It has been long known that other oxidative reagents could successfully release the gold from the tellurium bond, rendering it suitable for conventional cyanide leaching.

Roasting is the simplest-such oxidative process, where the tellurides are decomposed, producing tellurium off-gas while leaving behind a gold residue. In roasting a considerable amount of gold deposition occurs on the internal walls and tuyères of the roaster resulting in a significant quantity of gold being *locked up* in the roaster. Such gold can only be accessed when the roaster is shut down and a lockup gold recovery program carried out. Such lockup can be significant depending upon the quantity of gold present as the telluride and must be accounted for in any metallurgical balance activities. Usually a lockup factor is incorporated into such calculations to account for this gold and reconciled after roaster gold cleanout, usually a 6–12 month period.

The amenability of gold tellurides to bio-oxidation was demonstrated by Cashmore and Clark (1998). They took mounted single grains of the mineral calaverite and subjected then to an active bacterial-leach solution at 35°C for 24 h. SEM micrographs of the individual grains were taken before and after leaching. The chemical composition of the grain surface was determined using SEM-EDX, which showed the elemental composition at selected points on the surface. The original surface showed a gold composition of 39%

(58% tellurium), whereas after oxidation by the bacterial-leach solution, the gold content had increased to 93% with all tellurium passing into solution. Further work by Climo *et al.* (2000) demonstrated that bacteria did not oxidize the tellurides directly but contributed to the process by oxidizing ferrous ions to ferric ions, the so-called *indirect method* of bacterial oxidation. They showed that rapid direct attack of calaverite crystals, similar to that achieved with bacterial oxidation, occurred with an acidic ferric sulfate solution. The role of the bacteria is to regenerate the ferric ions that oxidize the tellurides.

$$2Fe^{2+} + \tfrac{1}{2}O_2 + 2H^+ \rightarrow 2Fe^{3+} + H_2O \text{ (bacterially mediated)} \tag{3}$$

$$AuTe_2 + 8Fe^{3+} + 6H_2O \rightarrow Au\text{ (s)} + 2HTeO_3^- + 10H^+ + 8Fe^{2+} \tag{4}$$

Dziurdzak *et al.* (1989) investigated the pressure oxidation of flotation concentrate obtained from Kalgoorlie gold-telluride ores. The untreated concentrate, which contained 79 g/t gold, gave about 68% gold extraction by simple cyanidation. About 40% of the refractory gold was combined with tellurium and the balance was locked in sulfides.

The pressure-oxidation testwork covered a wide range of conditions and clearly showed that enhanced cyanide recoveries were possible by cyanidation of the treated concentrate after pressure oxidation. For example, after a concentrate sample was treated at 190°C with an oxygen overpressure of 1,060 kPa over a 1.5 h residence time, it yielded 95% recovery when cyanide leached. These autoclaving conditions are common in the gold industry and are similar to those used to process gold-bearing arsenopyrite flotation concentrate at Placer Dome's Campbell Mine in Canada.

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Chapter 40

Treatment of antimonial gold ores

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1. INTRODUCTION

Gold and antimony are associated in a number of gold ores with resulting complications in the gold extraction process. The principal mineralogical forms in which gold occurs in these ores are:

- metallic gold, free-milling or associated with silicate gangue;
- as metallic gold associated with stibnite [Sb_2S_3]; it will be seen from the processes used to treat such materials that the majority of the gold appears to be in the metallic form rather than interstitially in sulfide lattices;
- associated with arsenopyrite both as metallic gold and interstitially in the sulfide lattice; and
- as aurostibite [$AuSb_2$].

A problem often encountered in evaluating historic descriptions of processes treating antimonial ores is that the gold deportment with respect to the mineral suite present is not defined. Evidently this has a crucial impact on the treatment route selected.

2. FUNDAMENTALS

Stibnite [Sb_2S_3] is the principal antimony sulfide mineral associated with gold although berthierite [$FeSb_2S_4$] and gudmindite [FeSbS] have also been

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reported (Davies and Paterson, 1986). The chemistry of stibnite in oxygenated alkaline cyanide solutions is very similar to that of orpiment [As_2S_3] and has the effect of consuming both cyanide and lime. Oxidation products of stibnite under these conditions include antimonites ($HSbO_3^{2-}$), antimonates ($HSbO_4^{2-}$) and thioantimonates (SbS_3^{3-}) (Nicol *et al.*, 1987). In addition to consuming lime and oxygen the products of stibnite oxidation reactions also include sulfides (S^{2-}), thiosulfate ($S_2O_3^{2-}$) and thiocyanate (SCN^-) in solution.

Any change in cyanide consumption following an increase in the stibnite in the ore is related to the formation of thiocyanate as antimony does not form a cyanide complex.

The rate of oxidation of stibnite is strongly dependent on pH with appreciable dissolution at pH 10 reducing to low levels at pH 12. Fig. 1 shows Hedley and Tabachnick's (1958) results of the cyanidation of a synthetic ore containing 0.25% stibnite at pH values of 10, 11 and 12.

Sulfur containing anions such as thioantimonates (SbS_3^{3-}) and sulfides (S^{2-}) are known to be strong 'poisons' in the cyanidation of gold (Nicol *et al.*, 1987), and Fink and Putnam (1950) have shown that dissolved sulfide levels of as low as 0.5 mg/L can have a significant deleterious effect on rates of gold dissolution.

In many cases where minor stibnite is present, pre-aeration, addition of lead nitrate (to precipitate sulfide ions) and pH control around 10 can negate any adverse influences due to the stibnite.

Avraamides *et al.* (2000) argued that the use of stibnite in assessing the effect of antimony on gold dissolution made it difficult to differentiate between the impacts of antimony and sulfur species. They concluded that the

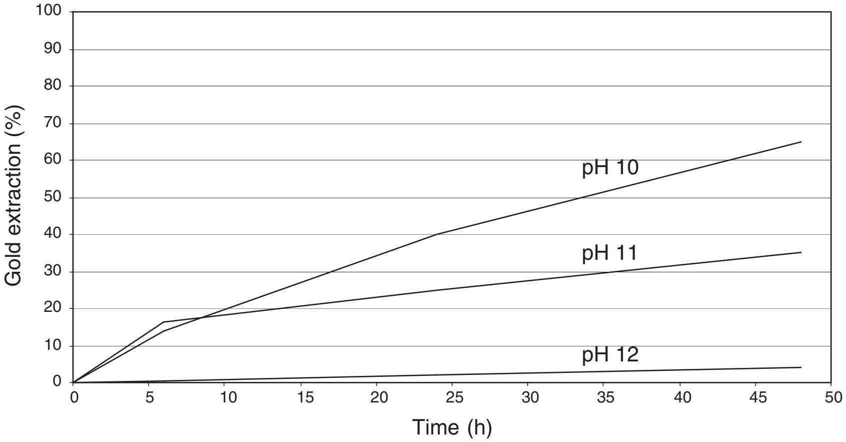

Fig. 1. Effects of gold extraction at pH 10, 11 and 12 (after Hedley and Tabachnick, 1958).

SbO^+ ion could also inhibit gold dissolution but only when the gold was in a relatively pure form. Their study on stibnite ore from the Big Bell mine concluded that conventional pre-treatment options and the addition of lead nitrate actually decreased the gold recovery from cyanidation.

Ores and concentrates containing stibnite have also been treated by roasting. This is generally required if significant amounts of the gold are present in a truly refractory form such as associated with arsenopyrite or as aurostibite. A two-stage roasting process, similar to that used for arsenic sulfide ores, can also volatilize antimony oxides and prevent adverse reactions such as the production of metallic antimony, which can coat the surface of gold particles (Nagy *et al.*, 1966) or the formation of silver glasses in high-silver ores (Matsukawa *et al.*, 1956).

Aurostibite is a completely refractory mineral, which has conventionally been successfully treated by roasting such as at Giant Yellowknife (Halverson, 1990). However, roasting of refractory concentrates is becoming increasingly uneconomic due to environmental considerations, particularly as arsenic is frequently associated to a greater or lesser extent with antimonial ores.

A recent investigation by the author (Unpublished, 2003) into the recovery of gold from a flotation concentrate containing significant aurostibite indicated that recovery from this mineral could only be achieved by pressure oxidation or to a lesser extent by bio-oxidation. Intermediate approaches such as low-pH pressure cyanidation, thiourea leaching, elevated temperature cyanidation and low-temperature calcination had no impact on recovery of the gold associated with aurostibite.

Although tolerance limits of 80–300 mg/L Sb have been quoted (Marsden and House, 1992) for *thiobacillus ferrooxidans*, it is believed that bacterial cultures may well be able to be acclimatized to levels greater than this with prolonged exposure.

3. COMMERCIAL OPERATIONS

For ores containing small amounts of antimony with the gold present in a non-occluded form, pre-aeration combined with lead nitrate additions and alkalinity control around pH 10 will normally give satisfactory gold dissolution. Reference to Fig. 1 indicates that a pH below 10 may be justified in which case a low alkalinity leach technique using equipment such as a pipe reactor may be justified. This approach will be discussed further in the context of leaching stibnite concentrates at Consolidated Murchison at Gravelotte.

The most prominent examples of antimonial gold ores are the Hillgrove mine operated by New England Antimony Mines in New South Wales, Australia and the Consolidated Murchison Mine originally operated by

Johannesburg Consolidated Investments and now owned by Metorex, at Gravelotte in Limpopo Province, South Africa.

At both of these operations, free gold is separated by gravity concentration and separate arsenopyrite and stibnite concentrates are produced by flotation. At both operations a significant amount of gold reports to the arsenopyrite and a pressure oxidation circuit was installed to treat this stream at Hillgrove in 1999 (Johns *et al.*, 2002).

The philosophy is adopted at both mines of recovering gold from the stibnite concentrate without oxidation and with subsequent sale of the gold-depleted stibnite. This is a consequence of the lack of gold credits available from antimony smelters on concentrate purchased by them.

3.1. Hillgrove

At Hillgrove, 10–20% of the gold in the plant feed reports to the stibnite concentrate, 35–50% to the arsenopyrite concentrate and 10% is recovered by gravity (Johns *et al.*, 2002). That a significant amount of the gold can be recovered in this way implies that most of the gold present in the stibnite concentrate is in the form of metallic gold and is not contained interstitially in the sulfide lattice.

At Hillgrove, gold is recovered from the antimony concentrate by thiourea leaching (Hisshion and Waller, 1984). Antimony concentrates usually assay 30–40 g/t gold and are leached on a batch basis, of approximately 8 t/8 h. Leaching is rapid and occurs in less than 15 min with pH, redox potential and thiourea concentration being critical to process control. Due to rapid reduction of redox potential in the leach, relatively high thiourea and ferric ion concentrations are used. Gold is recovered from the leach solution on activated carbon and the redox potential of the barren solution is adjusted back to a suitable level for leaching with hydrogen peroxide.

Gold recovery from the stibnite concentrate is in the range 50–80%, dependent on the level of exposure in the concentrate treated.

3.2. Consolidated Murchison

The operation at the Consolidated Murchison Mine has been comprehensively described by Davis and Paterson (1986). At the time of their paper, approximately 35% of the gold in the plant feed was recovered by gravity separation and a further 35–40% reported to the stibnite concentrate, resulting in a concentrate gold grade of around 30 g/t. Variable levels of aurostibite are reported to be present in the feed to the plant but no indication is given as to where this mineral reports in the plant products.

Gold is recovered from the stibnite concentrate by a low alkalinity, high-pressure cyanidation process operated in a 1.5-km-long pipe reactor. The reactor was originally designed to treat 1,000 t/month of antimony concentrates on a batch basis.

Concentrates at 55% solids are pre-screened at 2 mm and conditioned with 1.4 kg/t of lead nitrate for 30 min in a pachuca (P1) holding a batch of 20 to 22 t. Lime is added to raise the pH to 7 if necessary and sodium cyanide equivalent to a 2% solution (19 kg/t of solids) is added just prior to transferring the slurry to a second pachuca (P2).

Slurry is pumped from P2 back to P1 using a high-pressure piston pump via the pipe reactor. The reactor comprises 16 straight lengths, each 85 m long, of schedule 40, 50 mm NB pipe. Pressure is maintained in the reactor by a ceramic choke at the discharge end and a smaller choke recycling slurry from the feed pump discharge to the feed pachuca. Pressure at the start of the reactor is typically 8.8 MPa.

Oxygen is added 10 m downstream of the feed pump at a pressure of 12.0 MPa. Oxygen consumption averages 57 kg/t over the two passes. The average pH of the process slurry has been found to be 9.8.

Each batch of material is treated twice through the pipe reactor, the second pass improving gold dissolution by a further 5–9%, giving a total of just less than 80%. The cyanide level is adjusted back to 1% if it has fallen below this level, between the two passes through the pipe reactor.

The reactor has a residence time of around 15 min with a slurry velocity of 1.67 m/s, treating a batch of concentrate in 135 min.

4. NEW PLANT DESIGN

For gold ores where minor, economically insignificant stibnite occurs it is difficult to be prescriptive concerning the optimum flowsheet because stibnite is seldom the sole problem mineral, with arsenopyrite and similar minerals nearly always being present.

If low levels of stibnite constitute the only cyanidation problem then pre-aeration, lead nitrate and controlled alkalinity around pH 10 will normally be adequate to ensure satisfactory recovery in conjunction with a typical CIL circuit applicable to free-milling gold ores.

If the ore behaves as in Fig. 1 (higher dissolutions at lower pH values) and the head grade is sufficiently high, then low-pH pressure cyanidation may warrant investigation.

For removal of gold from stibnite concentrates which will be subsequently sold to a smelter, both thiourea leaching and low alkalinity, high-pressure cyanidation may be applicable. For similar recoveries, economics will probably tend to favour thiourea where the scale of operation is small and cost of capital is high.

It is noticeable that Davies and Paterson (1986) comment that reactor residence time at Gravelotte was considered inadequate and that plant results did not match those from the laboratory testwork. The laboratory work was carried out in autoclaves rather than pipe reactors (Muir *et al.*, 1984) and the plant residence time of 30 min, after two passes, is considered to be close to the economic break-even point between pipe reactors and autoclaves.

The investigation of using autoclaves rather than pipe reactors may then be justified in the investigation of the applicability of the low alkalinity, high-pressure cyanidation process.

Stibnite and aurostibite may be components of a refractory sulfide concentrate, in which case any gold associated with the stibnite would be able to be recovered using one of the processes outlined for stibnite concentrates but gold intimately associated with pyrite or arsenopyrite would be unaffected. Gold associated with aurostibite can be recovered in processes conventionally used for refractory sulfide concentrates such as pressure oxidation, roasting or bacterial oxidation. Of these, roasting is frequently difficult to accommodate on environmental grounds and bacterial oxidation may be adversely impacted depending on the tolerance of the culture used to the prevalent antimony levels in solution. It can therefore be concluded that pressure oxidation will frequently have the least process risk but bacterial oxidation cannot be ruled out without recourse to testwork.

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III.3 *Summary of gold Plants and Processes*

Developments in Mineral Processing, Vol. 15
Mike D. Adams (Editor)

Chapter 41

Summary of gold plants and processes

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1. INTRODUCTION

The concept of a generic flowsheet for the processing of gold ores may seem to have been superseded, given the foregoing discussion of many unit operations and process configurations. However, taking the view that simplifying the complexity can assist the process engineer or metallurgist, an overview prior to filling in the detail often reveals that certain process steps must necessarily precede others.

Given the variable mine life of gold plants, from many years to just several months, there is no point in attempting a comprehensive snapshot summary of all current gold plants. Therefore, the approach in this chapter is to provide a shortlist giving examples of the many flowsheets and process issues in plants that have been referred to within this volume. In each case, reference is made to the chapters where more detailed discussion may be found.

2. SUMMARY OF GOLD PLANTS AND PROCESSES

The general principle behind the structure of the volume is that of flowsheeting based on unit operations and applied to a mineralogical classification of gold ore types. Typical unit operations associated with the generic process flowsheet embodied within the structure of this book are shown in Fig. 1. Whether gold is the primary value metal or part of a suite of metals such as nickel, cobalt, copper or platinum-group metals (PGMs), selection of an appropriate combination of these units would likely result in a usable flowsheet.

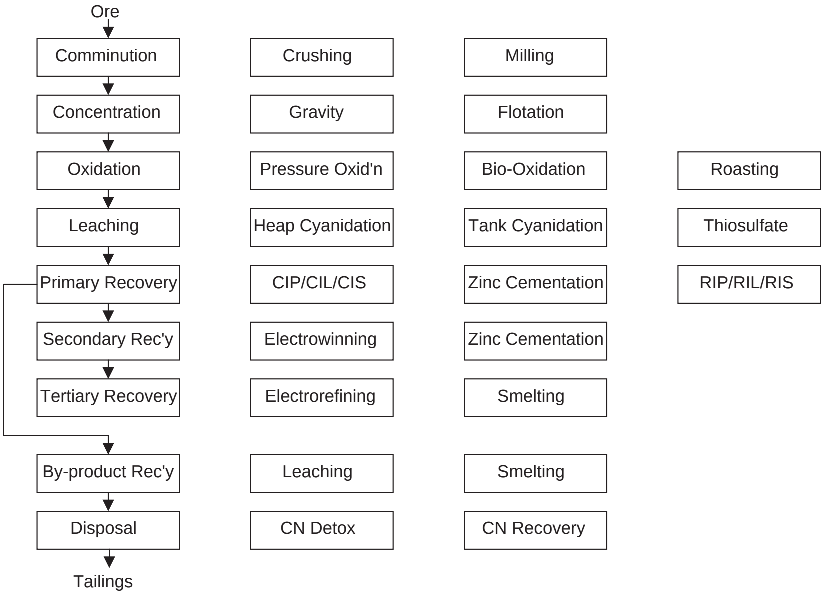

Fig. 1. Generic flowsheet for processing gold-containing ores.

Selection of the most appropriate unit operations for a given project entails a careful mineralogical and metallurgical investigation. Assuming that such an investigation has been carried out on a representative sample of the ore in question and the principles outlined in the first part of this book are being applied, the selection process can be assisted by scrutinizing previous and current practical operating flowsheets. Table 1 provides examples of flowsheets and process issues in gold plants from this book.

3. CONCLUSIONS

The information in Table 1 has been captured from the chapters in this book. It is not intended to be more than a summary reference to get a flavour of the processes that operating gold plants have implemented to overcome the issues pertaining to their particular ore mineralogy, water chemistry and the many other site-specific factors that come into play.

Some key conclusions that can be drawn are as follows:

- Innovations in comminution unit operations are exemplified by those undertaken at Freeport, which is one of the largest gold mills in the world, despite being a copper mine. This highlights the ongoing trend towards gold recovery from more polymetallic and refractory deposits, as free-milling gold resources become depleted.

- Concentration of gold by both gravity and flotation has seen innovation driven partly by the development of new items of equipment, as well as their novel application within comminution and other circuits.
- Treatment of refractory ores has become increasingly important; pressure and bacterial oxidation as well as roasting technologies have increasing relevance to the modern gold metallurgist. Further developments that increase recoveries while decreasing reagent consumptions are set to continue, particularly in the development of complex flowsheets that target the recovery of both base and precious metals from refractory orebodies. As both the knowledge base and the number of applications increase, so the risk of applying these processes becomes smaller. The same can be said of other problematic ores, such as carbonaceous preg-robbing, tellurides and antimonial ores.
- Advances in cyanide leaching have clearly been made in the treatment of problematic ores such as those arising from oxidation processes and those containing complex mineralogies, including reactive sulfide or high-silver ores. While there has been much work on the development of alternative lixiviants for gold, such as thiosulfate, the ongoing initiatives in cyanide management, such as the Cyanide Code, and the inherent benefits of a reagent that, in a well-designed flowsheet, is low level and biodegradable, suggest that cyanide will continue to be applied for some time to come.
- Advances in the recovery of gold from leach solution have also been influenced by developments in equipment and reagents. Ongoing improvements in the refining of gold are also being made. Innovations such as the Anglo American Corporation (AAC) pump cell contactor and gold-selective RIP have found niche applications at a few operating plants.
- The future of cyanide in gold processing will also be influenced by the increasing application of cyanide detoxification or recovery processes into flowsheets; development of new technologies for the economic recovery and recycle of cyanide from plant tailings is continuing.
- Tailing-storage facility design has seen increased attention in recent years. Placement of paste or dry tailings using techniques such as centrally thickened discharge, for example, is an innovation that may address issues of dam stability as well as water and cyanide recovery, while resulting in a more natural looking landform on closure.

The principle of applying generic metallurgical flowsheeting based on unit operations to a mineralogical classification of gold ore types lies within the structure of this book; the summary presented in Table 1 exemplifies this premise. Detailed knowledge of the mineralogy of an orebody and the chemistry of the various process waters is the key to unlocking the wealth contained within.

Table 1
Summary of gold plants and flowsheets discussed in *Advances in Gold Ore Processing*

Plant	Location	Ore type	Unit process	Issue	Chapter
Consolidated Murchison Mine	South Africa		Cyanidation under high oxygen pressure	Recently used with tube autoclaves 1.5 km long and 5 cm inner diameter. Leaching at ambient temperature and ~5 MPa oxygen pressure and 0.2–0.5% NaCN; 15 min residence time for 85% recovery. Cyanide oxidation negligible	0
Grasberg and Kemess	Indonesia, Canada	Coarse/flaky gold, copper–gold	Column cells	Grind size	2
Kemess	Canada	Copper–gold	Flotation	Chloride ions and mercury act as depressants	2
Bulyanhulu	Tanzania		Contact float cell on Knelson tails	Gravity/flash float recovery increase	2
Phoenix	Nevada	Silver–gold	Flotation	Loss of Ag-free particles	2
Batu Hijau	Indonesia		Flotation	Mn enrichment with rejected Au	2
KCGM and Kumtor	Australia, Kyrgyzstan		Flotation	Calaverite [$AuTe_2$] floats more efficiently than metallic gold	2
Twin Creek	Nevada		Grinding and flotation	To avoid oxidation, carried out under nitrogen with lead nitrate	2
Carlin	Nevada		Flotation	Acidic conditions improved selectivity and kinetics	2
Donlin Creek	Alaska			Submicroscopic gold carried by arsenopyrite	2
Olympias	Greece			Submicroscopic gold shared by arsenopyrite and arsenic-rich pyrite	2
Cortez	Nevada			Surface gold on carbonaceous matter by sorption from gold-bearing hydrothermal solutions (natural preg-robbing)	2
Lihir	PNG		Pressure oxidation	Chloride ions from seawater seeping into the orebody can generate gold *tetra*chloride, which then is adsorbed and reduced to Au° on pyrite surfaces	2
Sheba	South Africa		Bio-oxidation	Five-fold increases in the rate of oxidation were noticed between arsenic-rich and arsenic-poor zones of arsenopyrite and between arsenopyrite and the arsenic-rich zones of pyrite	2
Bottle Creek, Pajingo	Nevada, Queensland	High-silver	Carbon-in-leach (CIL), elution, electrowinning (EW)	Require elevated elution temperature	3

Table 1 (*continued*)

Plant	Location	Ore type	Unit process	Issue	Chapter
Rawas	Indonesia	High-silver	CIL	Elution followed by zinc precipitation	3
Akjoujt	Mauretania	Gold–copper		Ammoniacal cyanide leachant	3
Beaconsfield	Tasmania			Acidification–volatilization–regeneration (AVR)	3
Telfer	Western Australia			Sulfidization–acidification–recycling–thickening (SART) process recovers both copper as sulfide and cyanide for reuse	3
Penjom	Malaysia			Kerosene (8 L/t) with a commercial ion-exchange resin to adsorb the gold	3
Salsigne	France			High oxygen demands; oxygen in the first two leach tanks; peroxide in the CIL; external aeration device	3
Minahasa	Indonesia	Mercury	Leach	Limit the cyanide addition	3
Bogosu	Ghana	Refractory sulfide		Concentrate roasting	3
Sansu, Ashanti Goldfields	Ghana	Refractory sulfide		Concentrate BIOX®	3
Three Mile Hill	USA	Refractory sulfide		Concentrate fine milling	3
Macraes Flat	New Zealand	Refractory sulfide		Concentrate fine milling/pressure oxidation	3
Kanowna Belle	Western Australia	Refractory sulfide		Concentrate roasting	3
Minahasa	Indonesia	Refractory sulfide		Whole-ore roasting	3
Bakyrchik	Kazakhstan	Refractory sulfide		Nitric acid oxidation	3
Golden Spec	Western Australia	Refractory sulfide		Pressure cyanidation	3
Kanowna Belle	Western Australia		Roasting	Improved recovery from roasting over biological oxidation	3
Youanmi	Australia		Bio-oxidation	Occurrence of gold with arsenopyrite and not with less reactive sulfide minerals such as pyrite; low degree of sulfide oxidation for maximum gold recovery	3
Twin Creeks, Macraes	Nevada, New Zealand	Refractory sulfide, Preg-robbing		Newmont's high temperature pressure oxidation process on finely ground concentrates; temperature, oxidation–reduction potential (ORP) and acidity are closely controlled in the autoclave to the oxidize sulfides and passivate carbonaceous material	3
Macraes	New Zealand	Preg-robbing	Carbon-in-pulp (CIP)	Sub-micron carbonaceous platelets causing preg-robbing	3
Bakyrchik	Kazakhstan	Preg-robbing		Separation of preg-robbing material by physical techniques prior to oxidation	3

Sansu	Ghana	Preg-robbing	Bio-oxidation	CIL to treat carbonaceous BIOX® product	3
Wiluna	Western Australia			Availability of good quality carbonates close to the mine	3
Minahasa	Indonesia		Roasting	Whole-ore roasting	3
Sunrise Dam	Western Australia		Crushing, ball milling, CIL	High salinity of process water – pH and cyanide measurement and on-line control, modified alkali dosing, on-line HCN gas measurement	8
PT Freeport	Indonesia		Crushing, milling	Improved fragmentation can also lead to higher shovel and haul truck productivity, reduced boulder handling/secondary blasting costs and higher primary crusher utilization	12
Alumbrera	Argentina		Crushing, milling	152 mm steel increased throughput for hard ore types compared to a 127 mm make-up ball	12
Batu Hijau	Indonesia		Crushing, milling	Retrofitted semi-autogenous grinding (SAG) screens to supplement trammels	12
Ridgeway, Cadia	Australia		Crushing, milling	Circuit screening trommel oversize at Ridgeway after the trommel-only circuit at Cadia resulted in difficulties with the pebble crushing circuit	12
Kennecott Utah, Copper Alumbrera	Utah, Argentina		Crushing, milling	Large SAG operations with water cannon return; trommel oversize is returned directly to the mill with a water jet; retrofit pebble crushing is significantly more complex	12
Mission Complex	Arizona		Crushing, milling	Pebble stockpile	12
PT Freeport	Indonesia		Crushing, milling	Flexibility to return SAG feed an option to balance the SAG and ball-mill circuits during periods of ball-mill limitations	12
Louvicourt	Quebec		Comminution, flash flotation	Flash flotation on cyclone underflow	12
Cadia Hill, Telfer	Australia		Comminution, flash flotation	Gravity and flash flotation circuits combined or integrated	12
Carlin, Goldstrike	USA		Roasting, dry grinding	Roaster facilities fed by Krupp double-rotator dry mills	12
Minahasa	Indonesia		Dry grinding	Aerofall SAG mill followed with dry ball-milling	12
Round Mountain, Marvel Loch	Nevada, Western Australia		Gravity	Rotating gravity devices	13
St. Ives and Kundana, Porgera, Dome Mine	Western Australia, Papua New Guinea, Ontario		Gravity, intensive cyanidation	Recent retrofitting of intensive cyanidation in gold rooms; additional overall recoveries of 0.5–1.5%	13
Penjom	Malaysia	Preg-robbing	Gravity, intensive cyanidation	Combination of gravity-recoverable gold (GRG) and gold carrier gravity recovery followed by	13

Table 1 (*continued*)

Plant	Location	Ore type	Unit process	Issue	Chapter
				intensive cyanidation contributed to ~20% increase in overall gold recovery	
Beaconsfield	Tasmania		Gravity	InLine Pressure Jig on mill discharge/cyclone underflow and centrifugal concentrator. In parallel, a Knelson Concentrator circuit	13
Bjorkdal, Omai	Sweden, Guyana		Gravity	Reichert Cones on leach tails	13
Granites, Round Mountain	NT, Australia, Nevada		Gravity	Spirals on cyclone underflow	13
Beaconsfield	Tasmania		Gravity, flash flotation	Gravity recovery co-currently with flash flotation	13
St. Ives	Western Australia		Milling, gravity, intensive cyanidation	Coarse grind; InLine Pressure Jigs with Falcon SB in the grinding circuit to recover both GRG and gold carriers. Expect ~35% overall recovery increase. InLine Leach Reactor (ILR)	13
Jubilee Gold	Western Australia		Gravity	Recovery of GRG from jig concentrate with Gekko Spinner	13
Kettle River	Washington		Gravity	Recovery of GRG and non-GRG from cyclone overflows with Falcon continuous concentrator. Increases of up to 5% recovery	13
Granny Smith	Western Australia		Gravity	Recovery of GRG and non-GRG from cyanidation residues with cyclones and Kelsey jig. Increases of up to 4% recovery	13
Bulyanhulu	Indonesia		Gravity, flotation	Contact cell competing with two Knelson Concentrators lowered the gravity recovery by floating fine GRG. Gravity recovery restored when rotating velocity was slowed down and a regrind mill commissioned in the gold room	13
Fimiston	Western Australia		Gravity	Gravity recovery to minimize GRG coarser than 100 μm reporting to the cyclone overflow. Finer classification and GRG would have favoured flash flotation	13
St. Ives	Western Australia		Gravity, intensive cyanidation	Low-volume/high-grade gravity and flotation concentrates by batch ILR	13
Bibiani	Ghana		Gravity, intensive cyanidation	High-volume gravity and flotation concentrates treated by continuous ILR	13
Union Reef	Western Australia		Gravity, intensive cyanidation	High-grade gravity concentrates treated by Acacia Reactor	13

Three Mile Hill	Western Australia		Flotation	Lead nitrate activator for preferential flotation of arsenopyrite from pyrrhotite	14
Surcease	California		Flotation	Lead acetate activator to produce bulk sulfide concentrate for roasting	14
Los Pelambres	Chile		Flotation	Float tailing treatment using NaHS recovered 30–45% of the unfloated gold; ~7% increase in gold recovery	14
Harbour Lights	Australia		Flotation	Differential flotation circuit separating pyrite from arsenopyrite; selective depression of arsenopyrite with potassium permanganate. Gold-carrying arsenopyrite concentrate shipped to a base-metal smelter	14
Three Mile Hill	Western Australia	Pyrrhotite	Flotation, cyanidation	High-cyanide consumption and slow gold leach rates. Pre-aeration included ahead of the flotation circuit; preferential flotation separation of arsenopyrite and pyrite from pyrrhotite. Lead nitrate was added as an activator	14
Freeport	Indonesia	Copper–gold	Flotation	Aerofloat 7249 provided a 4.5% improved gold recovery	14
Kemess	Canada	Copper–gold	Flotation	3477 in the cleaner scavenger circuit improved the recovery of tarnished flaky gold. 20–100 µm particle-size free gold floated rapidly in the first three rougher cells; 5–20 µm gold particles floated at a slower rate; coarser gold (> 100 µm) was recovered in the first two rougher and last rougher-scavenger cells	14
São Bento	Brazil		Flotation, pressure oxidation, bio-oxidation	Gold and pyrite floated into a bulk concentrate for further processing by bacterial and pressure leaching	14
Morro Velho	Brazil	Graphitic–pyritic	Flotation, roasting	First stage of flotation to remove free gold and graphite with mercaptobenzothiazole at neutral pH. Second stage to recover gold-containing pyrite with *di*thiophosphate. Roasting of combined concentrate	14
Lone Tree, Twin Creeks	Nevada	Fine-grained arsenian pyrite	Flotation	Floated using N_2TEC technology at neutral pH values with lead nitrate as activator and xanthate as collector	14
Campbell	Ontario	Arsenopyrite–pyrite	Flotation, pressure oxidation	Flotation with copper sulfate as activator, potassium amylxanthate (PAX) and AF208 as collector and Dowfroth 250 as frother at natural pH. Flotation concentrate is pressure leached	14

Table 1 (*continued*)

Plant	Location	Ore type	Unit process	Issue	Chapter
Snip	British Columbia, Canada		Flotation	Floatation at natural pH using Aerophine 3418A, *di*thiophosphate and Dowfroth 250 frother. Concentrate sent to a smelter	14
Porgera	Papua New Guinea	Pyrite–arsenopyrite	Flotation, pressure oxidation	Flotation at natural pH; PAX as collector; frother is a mixture of methyl isobutyl carbinol (MIBC) and Dowfroth 400. Flotation concentrate is pressure leached	14
Macraes	New Zealand	Arsenopyrite–pyrite–pyrrhotite	Flotation	Bulk sulfide flotation concentrate at natural pH with copper sulfate, sodium isobutyl xanthate (SIBX) collector, *di*thiophoshate promoter; MIBC and Interfroth 60 frothers	14
Wiluna	Western Australia	Arsenopyrite–pyrite	Flotation, bio-oxidation	Bacterial oxidation to process bulk flotation concentrate prior to cyanide leaching. Flotation at pH 8.2 using copper sulfate, PAX and Interfroth 50	14
Beaconsfield	Tasmania	Arsenopyrite–pyrite	Flotation	Unit flotation cell in milling circuit. Copper sulfate is added to the mill; SIBX to different three locations in the flotation circuit	14
Kanowna Belle	Western Australia	Arsenopyrite–pyrite	Flotation, roasting	Flotation at natural pH values with copper sulfate, PAX and a guar gum depressant. Combined flash flotation concentrate, first rougher concentrate and rougher–cleaner concentrate that contains pyrite and arsenopyrite is roasted	14
Ashanti	Ghana		Flotation, bio-oxidation	Combination of column and mechanical flotation cells to produce a bulk concentrate for bacterial leaching	14
Fairview	South Africa		Flotation	Flotation at natural pH with SIBX or thiocarbamates as collector	14
Sheba	South Africa		Flotation	Flotation at natural pH with SIBX or thiocarbamates as collector. Copper sulfate is also used at the Sheba flotation plant	14
Emperor	Fiji	Telluride	Flotation, roasting, cyanidation	Lime added to the grinding circuit to depress sulfide minerals. Selective flotation of telluride minerals with *poly*oxypropylene glycol ether frother at pH 9. Cleaning of telluride concentrate with sodium silicate as gangue slime depressant and froth modifier. Soda ash addition to flotation tailings at pH	14

				9.5 prior to conditioning with xanthate and Terric 402 frother and then floating a sulfide concentrate; reground before cleaning, roasting and cyanidation	
KCGM	Kalgoorlie	Sulfide–telluride	Flotation, roasting, cyanidation	Bulk concentrate for roasting; using copper sulfate, xanthate and frother	14
Vaal Reefs	South Africa		Flotation	Copper sulfate, Aeropromoter 407; pH 7–8.5	14
Chemwes	South Africa	Residue retreatment	Flotation	Copper sulfate, SIBX; pH 7–8.5.	14
Ergo	South Africa	Residue retreatment	Flotation	Blended thiol collector; pH 7–8.5.	14
Sonora	California	Pyrite, talc	Flotation	Xanthate and Aero 5688 promoter with small additions of depressant	14
Rio Paracatu Mineração (RPM)	Brazil	Pyrite, arsenopyrite	Flotation cyanidation	Flotation with copper sulfate and xanthate; concentrate is reground before cyanidation.	14
Royal Oak	Ontario	Pyritic	Flotation cyanidation	Flotation with PAX, *di*thiophosphate and Dowfroth 250; concentrate reground to 38 μm prior to pre-aeration and cyanidation	14
Stawell	Victoria	Carbonaceous pyrite–pyrrhotite, arsenopyrite	Flotation cyanidation	Flotation with copper sulfate, PAX and Terric 407 frother; concentrate reground before cyanidation	14
Goldstrike	Nevada	Carbonaceous/sulfide	Pressure oxidation, roasting, CIL	50% of gold in refractory carbonaceous sulfides. Sulfuric acid to remove carbonates prior to autoclave. Whole-ore acidic leach	15
Mercur	USA	Fine gold with sulfides and organic carbon, carbonates	Pressure oxidation, CIL	Whole-ore alkaline leach due to high carbonates	15
Campbell	Ontario	High As and S	Pressure oxidation Counter-current decantation (CCD), CIL	Concentrate acidic leach	15
Tonkin Springs	Nevada		Bio-oxidation	Whole-ore stirred reactor	16
Beaconsfield	Tasmania		Bio-oxidation	High degree of oxidation in 5–6 days at 42–50°C	16
Laizhou	China		Bio-oxidation	Filtration of precipitate, resulting in reduction in volume for tailings disposal and allowing recycle water for direct reuse. 95% sulfur oxidation; 97% gold recovery	16
Ashanti/Sansu	Ghana		Bio-oxidation	95% sulfur oxidation; 93–96% gold recovery	16
Wiluna	Western Australia		Bio-oxidation	90% sulfur oxidation; 94–98% gold recovery	16
Youanmi	Western Australia		Bio-oxidation	32% sulfur oxidation; 90–95% gold recovery	16
Vaal Reefs	South Africa		Bio-oxidation	49% sulfur oxidation; 85% gold recovery	16
Olympias	Greece		Bio-oxidation	34% sulfur oxidation; 55% gold recovery	16
Giant Yellowknife	Canada	Stibnite	Roasting	Fluidized-bed roasters to replace multiple-hearth roasters; increase in throughput. Stibnite	17

Table 1 (*continued*)

Plant	Location	Ore type	Unit process	Issue	Chapter
				oxidizes, causes clinkering of the concentrate. Control of Sb and S levels in feed	
Independence Mining	Nevada		Roasting	Oxygenated roasting in fluidized beds (3 units)	17
Barrick Goldstrike	Nevada	Carbonaceous refractory sulfide	Roasting	Oxygenated roasting in fluidized beds (2 units)	17
Cortez	Nevada	Refractory sulfides	Roasting	Circulating fluid-bed roaster, with air or oxygen enriched air, with partial calcine recycle. Calcine to for gold recovery by cyanidation	17
Gidji	Kalgoorlie	Refractory sulfides	Roasting, CIL	Circulating fluidized bed (CFB) (2 units); ~95% gold recovery	18
Cortez	Nevada	Carbonaceous	Roasting, CIL	Whole-ore CFB roasting	18
Newmont	Nevada	Refractory sulfides	Roasting, CIL	CFB roasting; mercury removal. Sulfuric acid plant. Gold recovery ~91%	18
Minahasa	Indonesia		Roasting	CFB roasting. Gold recovery ~93%	18
Carlin, Goldstrike, Twin Creeks	Nevada	Oxide	Heap leach	Coarse-crushed (75 mm) oxidized ores typically 70% recovery	19
Round Mountain	Nevada	Low sulfide	Heap leach, gravity, cyanidation	150,000 t/d low-grade sulfide heap leach; 30,000 t/d high-grade oxide 12 mm heaps; 12,000 t/d unoxidized ore by gravity separation and cyanide leaching in stirred tanks	19
Filon Sur, Hassai	Spain, Sudan	Iron oxides (oxidized massive sulfides)	Heap leaching	Soft and permeable; crushing to 75 mm; agglomerated with cement; conveyor stacked	19
Coeur–Rochester, Comco	Nevada, Bolivia	High-silver	Heap leaching	Nearly pure silver heap-leaches. Silver recovery is significantly less than that of gold	19
Illinois Creek, Brewery Creek	Alaska, Yukon		Heap leaching	Located near the Arctic Circle and experience temperatures of −30°C	19
Comco, Yanacocha and Pierina, Refugio	Bolivia, Peru, Chile		Heap leaching	Located at altitudes above 4,000 m (13,000 ft)	19
Hassai	Sudan		Heap leaching	Normal daytime temperatures $>50^\circ$C; annual rainfall <20 mm	19
Sansu	Ghana		Heap leaching	Very large solution surge ponds required	19
Geant Dormant	Quebec	Pyrrhotite, marcasite, pyrite	Cyanidation	Pre-aeration with lead nitrate for reactive sulfides	20
Fort Knox	Alaska	Low-sulfide ore, stibnite	Gravity, cyanidation	Recovery decreased by minor metallic sulfide content; increased with lead nitrate addition	20
New Britannia	Manitoba	Pyrite, arsenopyrite	Cyanidation		20

				Lead nitrate addition and cyanide-level control improved gold recovery; cyanide consumption drop	
Musselwhite	Ontario	Pyrrhotite	Cyanidation	Lead nitrate, oxygen with cone spargers, on-line cyanide analysis	20
New England Antimony	Australia	Gold–antimony concentrate	Thiourea leaching	Small-scale industrial application of thiourea leaching, with gold recovery on activated carbon	21
Elandsrand	South Africa		Merrill–Crowe	Relatively recently constructed; two-stage rotary-drum filtration, hopper clarification and zinc cementation with candle filters. The backwashed precipitate to a pre-coated rotary-drum filter and continuous-belt calciner	24
President Brand	South Africa		Zn cementation	Gold recovery from eluates as well as from solutions originating from intensive cyanidation	24
Nickel Plate	Canada		Merrill–Crowe	High soluble-copper values	24
Coeur–Rochester, Paradise Peak.	Nevada		Milling, heap-leach, Merrill–Crowe	Major US applications of zinc cementation	24
Pierina, Alto Chicama, Yanacocha, Maqui–Maqui	Peru		Merrill–Crowe	Larger recent applications of zinc cementation	24
La Coipa, Guanaco	Chile		Merrill–Crowe	Recent applications of zinc cementation	24
Veladero	Argentina		Merrill–Crowe	One of the largest Merrill–Crowe plants to date; scheduled to be commissioned at 2,000 m^3/h in 2005	24
Ashanti	Ghana		Merrill–Crowe	Main African application of zinc cementation	24
Zarafshan	Uzbekistan		Merrill–Crowe, heap leach	Capacity of 1,065 m^3/h	24
Muruntau	Russia		Resin-in-pulp (RIP)	Treated around 1.3 Mt of ore per month; AM2B resin; thiourea elution	25
Golden Jubilee	South Africa		RIP	Conventional CIP/CIL plant retrofitted to RIP resin-in-leach (RIL) plant owing to the low gold recoveries obtained with carbon. Conventional strong-base resin (A161RIP); zinc–cyanide elution	25
Barbrook	South Africa	Carbonaceous preg-robbing ore	RIP	Uses AAC pump cells and Minix resin; thiourea elution with EW	25

Table 1 (*continued*)

Plant	Location	Ore type	Unit process	Issue	Chapter
Penjom	Malaysia	Carbonaceous preg-robbing ore	RIP	Conventional CIP/CIL plant retrofitted to RIP/RIL plant owing to the low gold recoveries obtained with carbon. Uses Minix resin; thiourea elution with EW	25
Connemara	Zimbabwe		Resin-in-solution (RIS)	Vitrokele 912 strong-base resin	25
Fimiston	Western Australia		Roasting, CIP, EW	Expansion and conversion from conventional steel-wool cathodes to woven stainless-steel with an all-sludge bullion-handling system. Variable gold in solution	26
Pajingo	Queensland		CIP, EW	Arranging the anodes and cathodes in a rigid array to improve connections and uneven current and voltage distribution	26
Kloof	South Africa		EW	Kemix Sludge Reactor (rotating cathode) produces 3 t/month gold	26
Rand Refinery	South Africa		Refinery	High-speed silver-electrolysis (HSSE) plant for silver refining	27
DeLamar, Cerro Vanguardia	Idaho, Argentina		Cyanidation, AVR	AVR plants originally built to handle tailings slurry, but subsequently converted to solution treatment due to severe scaling	29
Golden Cross	New Zealand		Cyanidation, Cyanisorb	Gold loading on carbon enhanced by lowering cyanide strength and pH. Seepage from tailings pond discharged directly to river 18 months after plant closure	29
Rio Paracatu, Cerro Vanguardia	Brazil, Argentina		Cyanidation, Cyanisorb	Currently operating Cyanisorb process	29
Bulyanhulu	Tanzania		Tailings	Water-reducing (paste) surface tailings management system (scarcity of water; underground backfill	30
Omai, Baia Mare, Merriespruit	Guyana, Romania, South Africa		Tailings	Tailings-storage structure failures caused in part by standing water on the dams	30
Henty	Tasmania		Tailings	Total tailings product (potentially acid-generating) and other waste rock placed underground as paste backfill	30
Ergo	South Africa	Plant tailings	CIL	Gold recovery from a mixture of sulfide and non-sulfide bearing residues (sand and slimes dumps) from old mining activities	31

Akjoujt	Mauretania	Plant tailings, magnetite, soluble copper	Ammonia cyanidation	Tailings from TORCO process (heating refractory copper-oxides with NaCl and coal; flotation). Cyanidation recovery improved (75–88%) by oxygen gas injection in cyanidation	32
Mt Gibson	Australia	Laterite, soluble copper	Cyanidation	Viscosity and recovery problems; improved by draft-tube agitation, introduction of liquid oxygen with high-efficiency gas injector, as well as addition lead nitrate. Viscosity modifier added to the mill; lime added to leach feed. Copper recovered as sulfate by Sceresini process	32
Red Dome	Australia	Soluble copper	Cyanidation	Copper recovered as sulfide by Sceresini process	32
Telfer	Western Australia	Soluble copper	Cyanidation, SART	SART commissioned; only operated for a short time before Telfer entered care-and-maintenance phase	32
May Day	New South Wales	Soluble copper	Cyanidation	Elutech technology with commercial resin to recover gold, copper and base metals from cyanidation liquors. Copper eluted by oxidative-acid strip; copper recovery by solvent extraction (SX)/EW or as hydroxide; HCN scrubbing	32
Mt. Gordon	Queensland	Chalcocite–pyrite	Pressure oxidation, SX, EW	Recovers copper from ores or concentrates by low-temperature pressure leaching, copper SX-EW	33
Bagdad	Arizona	Cu concentrate	Pressure oxidation, CCD, SX–EW	Use of acid from autoclave oxidation of concentrates for a copper stockpile leach	33
Alliance Copper	Chile	Cu concentrate	Bio-oxidation	BIOCOP$^{\text{TM}}$ copper concentrates with extreme thermophile bacteria; copper recovery by SX–EW; 20,000 tpa Cu production plant	33
Sepon	Laos	Chalcocite with pyrite and clays	Leach, pressure oxidation, SX–EW	Under construction; atmospheric leaching; copper recovery by SX–EW. Barren washed tails floated to recover a pyrite/elemental sulfur concentrate, oxidized at 225°C to produce acid/ferric sulfate solution for atmospheric leach	33
Outokumpu	Finland	Chalcopyrite	Chlorination	Hydrocopper$^{\text{TM}}$ process; $\sim$1 t/d Cu demonstration plant. Counter-current leaching using air and chlorine. Residue (goethite and elemental sulfur) leached under controlled-potential conditions for gold; recovered on carbon or by precipitation. Copper solution purified by pH adjustment to precipitate cupric ion (recycle),	33

Table 1 (*continued*)

Plant	Location	Ore type	Unit process	Issue	Chapter
				cementation (silver), base-metal precipitation using sodium carbonate; IX for minor impurities. Cu precipitated as hydrated cuprous oxide for hydrogen reduction to metal	
Martha	New Zealand	High-silver	CIP	110°C Anglo American Research Laboratories (AARL) elution circuits operated without major difficulty	34
Pongkor	Indonesia	High-silver	CIP	15 g/t Au and 200 g/t Ag. Discharges the carbon advance stream onto a sieve bend to avoid slurry dilution. 110°C AARL elution circuits operated without major difficulty	34
Golden Cross	New Zealand	High-clay		Slurry would not thicken beyond 30% solids, making CCD expensive	34
El Peñón	Chile		Merrill–Crowe	Zn cementation selected because of environmental requirement to dispose of the tailings as a filter cake	34
Misima	Papua New Guinea		CIP	AARL elution run at two temperature levels to provide two eluates (high-gold and high-silver); nitric-acid silver leach; precipitated with NaCl and smelted to a high-silver bullion (~2% Au) and a high-gold bullion (50–70% Au)	34
Noranda	Quebec		Refinery	Anode-slimes treatment	35
Pori	Finland		Refinery	Anode slimes decopperized by oxidative leach; nickel removal by pressure leaching; selenium removal from the slimes, Doré smelting; electrolytic silver refining in a Moebius cell; gold mud purified by H_2SO_4 leach then dissolved in *aqua regia*; gold is recovered from solution by reduction (Na_2SO_3); and PGMs are cemented with iron	35
El Paso	Texas		Refinery	Anode slimes treatment by nitrate leaching of silver; gold SX	35
Inco	Sudbury; Acton	Ni/Co sulfides	Refinery	Anode slimes and carbonyl process residues; two-stage pressure leaching for Ni/Co and Cu/Se/Te. PGM concentrates from Ni and Cu circuits refined at Acton by *aqua regia*	35

				dissolution of Au, Pt, Pd and gold recovery from solution by reduction. SX introduced recently	
Falconbridge	Sudbury	Ni/Co sulfides	Refinery	Ni/Co recovery to pure metals using a chloride system; Cu roasted for conventional recovery from sulfate solution. Residue reduced to metal using hydrogen; chlorine leached under controlled redox potential; residue smelted to matte in an electric furnace, granulated and leached with HCl/Cl_2 to obtain the final precious metals product	35
Norilsk	Russia	Ni/Co sulfides	Refinery	PGMs recovered in anodic slimes from Ni/Cu circuits by roasting and leaching; residues combined in an electric furnace; anodes electrorefined. Anode slimes and copper precipitate both leached in sulfuric acid to generate PGM concentrates. New process includes atmospheric decopperization using matte to decopperize nickel anolyte; oxidizing atmospheric iron hydrolysis using nickel or sodium carbonate; pressure oxidation leaching; autoclave refining of copper concentrate	35
Minera El Toqui	Chile	Zn sulfides	Refinery	Pb/Au pre-float prior to Zn flotation; most gold in zinc concentrate or pyrite. Zinc metal is won from zinc sulfide concentrates via hydrometallurgical and some pyrometallurgical processes	35
Balen	Belgium	Zn sulfides	Refinery	Hot-acid leach residues floated to selectively recover a silver–gold concentrate using a standard sulfide promoter, followed by lead sulfate flotation using a laurylamine or sulfonate collector. Thiourea leach of precious-metal concentrate	35
Iijima	Japan	Zn sulfides	Refinery	98% of the gold reports as Cu–Pb–Ag leach residue that is floated to a Cu–Au–Ag concentrate	35
Zhuzhou	China	Zn sulfides	Refinery	Leach residues are also floated at this smelter. Direct cyanide or thiourea leaching of the zinc leach residue being considered.	35
Port Pirie	Australia	Pb	Refinery	Batch pyrometallurgical refining of lead bullion by Parkes process; zinc metal added to form alloys with the precious metals that are skimmed off	35

Table 1 (*continued*)

Plant	Location	Ore type	Unit process	Issue	Chapter
Amplats	South Africa	PGM concentrate	Refinery	Slow-cooled converter matte process (thermally insulated moulds). Iron concentrates the PGMs, free of such as arsenic, selenium and tellurium. Crushing and milling to liberate the iron-PGM phase; magnetic separation; concentrate leached to yield a final precious metals concentrate	36
Impala, Lonmin, Stillwater	South Africa, Montana	PGM concentrate	Refinery	Traditional matte water-granulation process; granulated matte counter-current leached with sulfuric acid for Ni; copper removal by pressure oxidation; leach residues are precious-metal concentrates	36
Sansu	Ghana	Carbonaceous, refractory pyrite–arsenopyrite	Bio-oxidation	Largest commercial biological-oxidation facility (790 tpd)	37
Kanowna Belle	Western Australia	Refractory low-sulfide (~1%), pyrite.	Flotation, Roasting, CIP	Two-stage concentrate roasting, with sulfur-dioxide discharge; 70–75% recovery raised to >97%. >200,000 mg/L total dissolved solids (TDS)	37
Macraes	New Zealand	Preg-robbing carbonaceous, pyrite–arsenopyrite	Flotation, Pressure oxidation, CIP	Cyclone desliming of rougher and scavenger concentrates to reduce preg-robber; milling and flotation circuits improved recovery of sulfides in coarser size-fractions, at coarser primary grind, particularly in column flotation	37, 38
Carlin	Nevada	Preg-robbing carbonaceous	Chlorination	Flash chlorination to deactivate carbon.	38
Jerritt Canyon	Nevada	Preg-robbing carbonaceous	Air oxidation, chlorination, CIL	Milled alkaline slurry treated by double oxidation, first with air at 70°C; the sulfuric acid produced was neutralized with lime. Second oxidation with chlorine ~20 h; residual chlorine destroyed; CIL. Gold recoveries of 90–93% chlorine consumption high if sulfide content >0.5%	38
Twin Creeks	USA	Preg-robbing carbonaceous	Pressure oxidation	Some gold soluble loss solubilization by chlorine from the processing water and precipitation on the carbonaceous matter. Addition of limestone, dolomite or proper ore blending overcame the problem. Operating at lower temperatures (~200°C) increased gold recovery	38

Beatrix	South Africa	Preg-robbing shale, phyllosilicates (pyrophyllite, muscovite, chlorite)	Cyanidation	Gold adsorbed and silicates decomposed under CIL conditions	38
Stawell	Australia	Preg-robbing carbonaceous		Inhibited preg-robbing by blinding the carbonaceous ore with diesel or kerosene (~200 mg/L); addition of kerosene suspended every few weeks (campaigning with non-preg-robbing ores) to restore the activity of the activated carbon	38
Goldstrike	USA	Refractory sulfidic carbonaceous	Roasting	Largest roaster (16,450 t/d). Six autoclaves for sulfide oxidation	38
Turquoise Ridge	USA	Refractory sulfidic carbonaceous	Pressure oxidation, CIL	Treats 1,800 t/d of ore in the Twin Creeks Sage Mill. Zinc precipitation on carbon eluate	38
Kumtor	Kyrgyzstan		Flotation, CIL	15,000 t/d; concentrate and tailings in parallel circuits. Gold recoveries ~76–80% depending on carbon content of the ore	38
Cripple Creek	Colorado	Telluride	Roasting	Whole-ore roasting; earliest tellurides to be treated	39
Wright–Hargreaves	USA	Telluride	Cyanidation, flotation, fine grinding	Cyanidation for non-refractory gold followed by filtration, flotation of residual tellurides, fine grinding of the concentrate in a pebble mill with high lime addition (12 kg/t). Concentrate cyanide leached for a prolonged time period and the leached pulp returned to the primary leach circuit; overall plant recovery > 96%	39
Emperor	Fiji	Telluride		Hypochlorite oxidation of high-grade gold telluride flotation concentrate (lime and cyanide to depress sulfides). $FeCl_3$ and MnO_2 oxidation were poor filtering. Residue cyanide leached (1.0–1.5% NaCN for 3–4 h); leach residue filtered, reacted with Na_2S, filtered and roasted. Tellurium precipitated from the chlorination liquor with Na_2S/Na_2SO_3; filtration, washing, drying, smelting to saleable tellurium metal ingots	39
KCGM	Western Australia	Telluride, Sulfide	Ultra-fine grinding, cyanidation	High dissolved oxygen (DO) levels not necessary for finely ground (~12 μm); 1–2 ppm DO reduced cyanide consumption whilst maintaining gold recovery. Thiocyanate levels dropped from > 1,000 to < 200 mg/L. Excess oxygen may also passivate gold by coating it with insoluble sulfide oxidation products	39

Table 1 (*continued*)

Plant	Location	Ore type	Unit process	Issue	Chapter
Giant Yellowknife	Canada	Refractory aurostibite	Roasting		40
Hillgrove	New South Wales	Arsenopyrite, stibnite	Gravity, flotation, pressure oxidation	Separate arsenopyrite and stibnite concentrates; significant gold reports to the arsenopyrite and a pressure oxidation circuit installed. Gold recovered from antimony concentrate by thiourea leaching	40
Consolidated Murchison	South Africa	Arsenopyrite, stibnite	Gravity, flotation, high-pressure cyanidation	Separate arsenopyrite and stibnite concentrates. Gold recovered from stibnite concentrate by low alkalinity, high-pressure cyanidation in a 1.5 km-long pipe reactor.	40

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Mike completed BSc (hons) and MSc degrees at Witwatersrand University in Johannesburg in 1983, before joining Mintek as a metallurgist. He completed a PhD degree in 1989 on the chemistry of the CIP process for gold recovery and joined Lakefield Oretest in 1999, from which he departed in 2004 as Metallurgical Manager. Mike is a Chartered Professional (Metallurgy) and has been awarded fellow status by the Australian and the South African Institutes of Mining and Metallurgy, as well as the Raikes gold medal by the South African Chemical Institute. He has published about 50 papers and 400 confidential technical reports and edited two books during an international consulting and research career in process and environmental metallurgy and chemistry.

Apart from ongoing work in gold, PGMs, zirconium and niobium, Mike's work over the last few years has focused mainly on the project management and metallurgy of integrated pilot-plant campaigns for definitive feasibility studies on the processing of nickel laterites and sulfides. These include BHP Billiton's Ravensthorpe Nickel in Western Australia, CVRD's Niquel do Vermelho in Brazil, Lionore's Tati Nickel in Botswana and Ivanplats' Syerston Nickel in New South Wales.

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