C.W. Ammen

Recovery And Refining Of Precious Metals

Second Edition

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and
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SECOND
EDITION

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To my wife, HAZEL
without her this book would have been impossible;
her contribution is immeasurable.

Contents

Introduction

This book is the product of 50+ years of hands-on physiochemical work with both ferrous and nonferrous metals and with the metallurgy of refining, extracting, and casting. Its purpose is to cover the various methods of recovery and refining of precious metals. Both primary sources (placer gold, black sand, and ores) and secondary sources (scrap jewelry, electronic scrap, old films, buffings, spent plating and stripping solutions, catalytic automobile converters, and old eyeglass frames) are covered.

The information contained in this volume is very basic and is intended for hands-on application and use. It is for nonchemist and chemist alike. I will not discuss the mathematical formulas for the various chemical reactions that take place—I leave them to the reader who wants to increase his working knowledge and understanding of chemistry. There are many courses offered in chemistry and extractive metallurgy, as well as a number of books available for self-study. The purpose of this book is to teach you how to perform various extractive, refining, and testing operations on precious metals (in various forms and states), with a resulting end product.

You will learn how to perform operations in assaying and extraction, qualitative analysis, quantitative analysis, testing, classifying, and concentration—some of a purely mechanical nature, some of a chemical nature.

Qualitative analysis involves the identification of an unknown material. To do this, you must have a plan of testing or attack. For example, is a given solution acidic, basic, or neither? With litmus paper you can quickly make this determination and proceed further. Again, assume you wish to identify a metallic material that is grayish white in color and seems to be heavy in relation to its size or amount. First, you boil a portion of it in water; nothing happens; therefore, it is insoluble in water. Next, you boil the sample in a solution of nitric acid; it is unaffected. You then boil it in aqua regia—one part nitric acid and three parts hydrochloric acid; it goes into solution. The material is, therefore, a member of the platinum group. By further treatment of the solution with various reagents (chemical substances used to produce a chemical reaction), you can pin down what it is.

In quantitative analysis, you know what the material is but wish to know the quantity. This procedure is much simpler and less time-consuming. A simple example would be a piece of metal that is an alloy of gold and silver. Silver is soluble in a nitric-acid solution; gold is not. You weigh the sample, boil it in nitric acid (putting the silver into solution), filter off the residue that remains undissolved (the gold), wash and dry it, and weigh. If the residue weighs 50% of the sample's weight prior to treatment, the alloy must be 50% gold by weight, and 50% silver.

There is a close relationship between qualitative and quantitative analysis. Suppose you were wrong in your first assumption that the material was an alloy of gold and silver; in reality, it was gold and copper, or gold and nickel. When you treated it with nitric acid, a green or blue solution would have resulted, indicating that the material other than gold was copper or nickel. In fact, you would have performed both a qualitative and a quantitative analysis.

Physical chemistry is our field. It is the study of the physical changes associated with chemical reactions and the dependence of physical properties on chemical compositions. Many chemical/physical and physical/chemical reactions are well understood; others are not. Although the nature of chemical and physical reactions is beyond the scope of this book, I will, where pertinent to the understanding of a chemical reaction, explain what happens in very basic terms.

In the study of the recovery and refining of precious metals one should spend some time reading all you can find on alchemy, early chemistry, and early metallurgy. See what was done and accomplished way back when. This will help you to understand what is being done at the present time. You will be amazed at how similar the methods used then and today are. "There is nothing new under the sun." In many cases you will find that some of the low-tech old-time methods are actually a better way to go. Man seems to like to complicate things which would be best left as is. Just look back to 1920. If you study Louis Dupare's method of breaking down crude platinum into its components (i.e., Os, Ir, Rh, etc.), in his paper "Le Platine Du Monde" ("The Platinum of the World"), it becomes very apparent that there are dozens of variations which could be used to accomplish this task. However, the simplicity of De Parc's method is low tech at its best.

The problem with bogus systems, equipment, and so-called secret formulas out there is real. It pays to examine any claims along these lines with a jaundiced eye.

You will find the study of the recovery and refining of precious metals very interesting and very consuming. If you become bitten by the "Gold Bug," there is no cure. Primary recovery of precious metals from ore or black sands is a costly adventure requiring lots of capital, equipment, and manpower. You are faced with satisfying a large group of various regulatory agencies, each of which seems as though it is unaware that the others exist. Even if you succeed in satisfying all of them, you are looking at years of paperwork and lots of bucks.

How much money do I need to start up a gold ore or placer mining operation?—an often asked question. The answer is quite simple. If you have enough money to do it, you do not need to do it. As an investor in a goldmining company and so forth, etc., you do not, in any case, use your food money or borrowed money. Use only money that you can easily lose without going bankrupt—money that is yours, not others.

Secondary refining is a case where it is possible with a fairly small investment you can turn a profit. This end of the business is played by the big boys also. However, if you keep it small and own it all, you can play on the sidelines and make some money.

In any case, even with a small secondary refinery, I would not give up my day job. Worked as a semihobby, one can do all right; and who knows it could grow in time to become your livelihood.

1

Primary Precious Metals

Primary precious metals are those found in nature as free metals, or in various compounds, such as oxides, or alloyed with another, as a base metal. Gold, for example, may be found free (but seldom pure) as nuggets, flakes, or very fine colloidal particles. It may also be found as part of a telluride compound. These natural telluride compounds are extremely important if found in large enough deposits, such as those at Cripple Creek, Colorado, and Goldfield, Nevada, and in Western Australia and Canada.

Ores

Ores vary widely in chemical and physical characteristics, and a goodly proportion of precious metals are by-products of the mining and refining of other, less noble metals. Apart from gold, silver, platinum, mercury, and a very little copper, few metals are found in significant quantities as native metals.

Methods of refining vary depending on the ore involved and the metallic value the operator is seeking. There is a definite crossover of technology from primary recovery to secondary recovery of precious metals. In fact, some processes of recovery and refining are exactly the same.

Consider the treatment of an ore for extraction of gold by the so-called "barrel process." In this process, the gold "values" are reduced to water-soluble gold chloride in a lead-lined rotating barrel (tumbler). The gold-bearing ore is roasted to eliminate any sulphides present. In this case, heat and oxygen serve as reagents. The sulphides are oxidized by being heated in the presence of oxygen, which produces sulphur dioxide. In any roasting operation, the by-products present an air-pollution problem and must be dealt with by precipitators or other means.

In large operations, the sulphur dioxide is used to produce sulphuric acid and other sulphide chemicals. Of course, this decision depends on the cost and market conditions. Sulphuric acid is a very widely used industrial chemical: over 70 billion pounds per year are produced in the United States alone. There are several methods of production. Contact process, using a vanadium pentoxide catalyst, and the "cat-ox" process are two such methods.

The roasted, sulphur-free ore is charged into the barrel with the bleaching powder (chlorinated lime). Some bleaching powders are mixtures of calcium chloride and hypochlorite (a salt of hypochlorous acid). When the roasted ore is in the barrel with the bleaching powder, sufficient water is added to cover them, and the barrel is rotated until its contents are well mixed; at this point, sulphuric acid is added, and the barrel is quickly closed and rotated.

The sulphuric acid oxidizes the bleaching powder, releasing the chlorine from the calcium chloride; the chlorine then combines with the gold values to form gold chloride, a water-soluble gold salt. The solution in the barrel, if evaporated, will form yellow to red crystals of auric chloride ($AuCl_3$). The time required to complete this action (gold recovery as a chloride of gold) depends on the gold content of the material being processed. Completion is judged by a quick test for gold in a sample of the material washed free of chloride. As with any process, the time and the amounts of bleach and sulphuric acid required depend on the size of the load, its gold content, and the physical setup. Each operator establishes these quantities for himself.

In this process, you must have an excess of free ("available") chlorine at all times, whether you know the precise quantity of gold you are working with or not. This is because the ore (or whatever) that is being treated is certain to contain—in addition to gold—some copper, silver, or other element capable of combining with chlorine to form a chloride. Thus, if you were to make the proportion of chlorine to gold in your solution exactly three to one (because $AuCl_3$ is one part gold to three parts chlorine), you would inevitably lose some chlorine to the other reacting metals, leaving you insufficient chlorine to combine with all the remaining gold. The way to avoid this wasteful result is to maintain an excess of available chlorine in the system.

The ore is roasted to rid it of sulphur, which in the form of sulphides (pyrites, for example) would combine with the added chlorine to produce sulphur chloride (S_2Cl_2) and/or sulphur dichloride (SCl_2). See Figure 1.1.

When the barrel is through being revolved, the drain is positioned at the barrel's gravitational bottom, and water is pumped under pressure into the top to leach out the gold chloride. See Figure 1.2.

The gold chloride molecules are in solution with water. If they were crystallized out by evaporation, their metal content would be about 58.1% of the crystals' total weight.

The gold chloride, dissolved in water, is stripped of its gold value by having sulphurated hydrogen gas (hydrogen sulphide—H_2S) bubbled through the solution. Hydrogen sulphide can be purchased in steel cylinders, or it can be generated by the action of a dilute sulphuric acid (1 volume of acid to 10 volumes of distilled

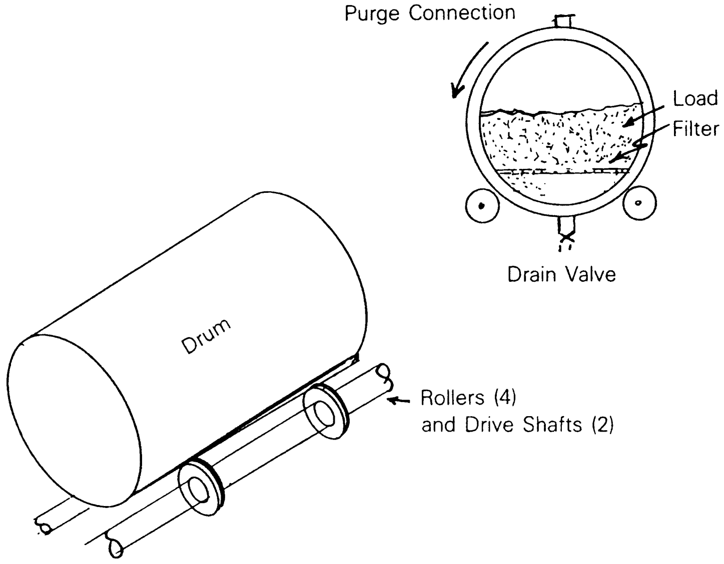


Figure 1.1. Basic chlorine barrel

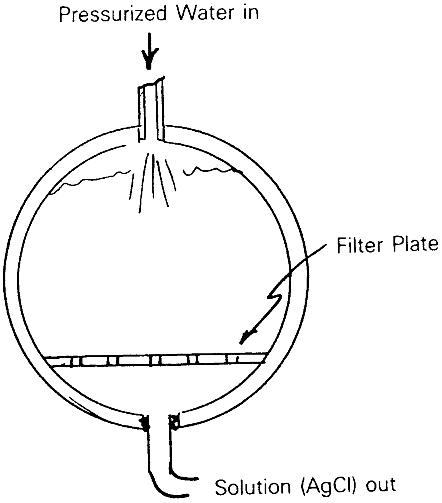


Figure 1.2. Purging the chlorine barrel

water) on iron sulphide. See Figure 1.3. Hydrogen sulphide is an extremely toxic gas—as toxic as hydrogen cyanide—and it is also flammable.

The gold is precipitated as a sulphide of gold. It is collected, dried, and roasted to drive off the sulphur, then treated with sulphuric acid to remove any copper or other metallic impurities that came down (precipitated) with the gold. After being washed well with hot water, it is again dried and melted with a little borax glass and a pinch of potassium nitrite. The next step depends on the degree of purity you are seeking. You might, for example, elect to re-refine the gold by wet chemical methods.

The simple barrel process described above, which is used to recover values from a primary source (ore), is also applicable to various types of material of a secondary nature, such as electronic scrap, plated ware, sweepings, and grindings.

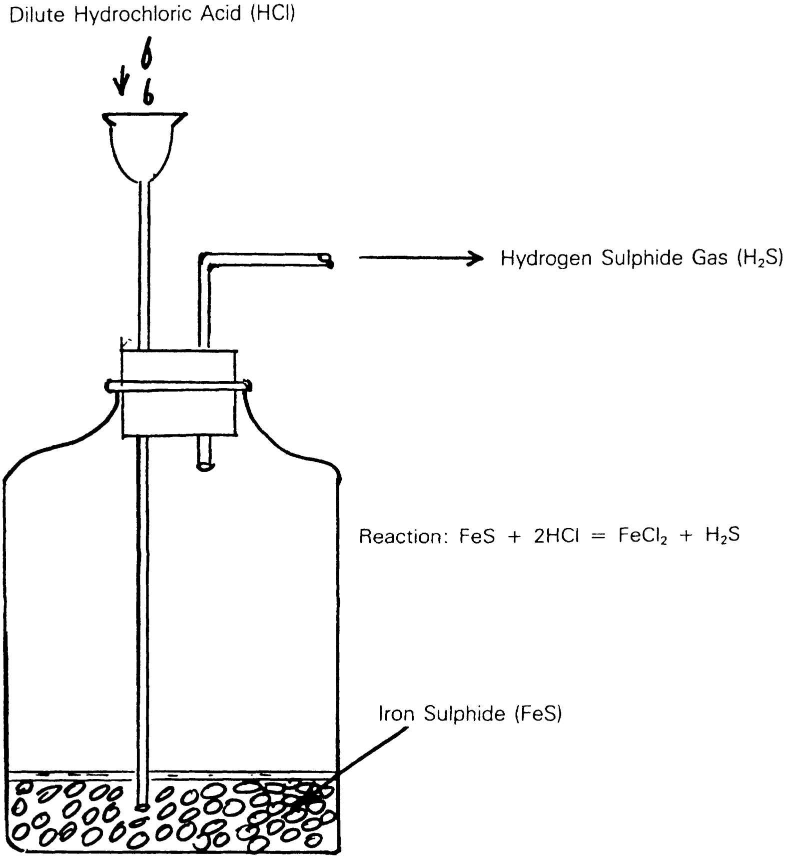


Figure 1.3. Simple hydrogen sulphide (H_2S) generation

It is an especially good process for refining electronic scrap—pin boards, circuit boards, and so on. After this material has been shredded and ground up, and after most of the organic material has been removed by burning or solvent extraction, a small barrel operation is an excellent way to recover the gold. The equipment is easy to build and inexpensive to operate.

A great percentage of the energy expended in the recovery of precious metal values from primary sources is spent on the physical recovery of the ore itself, by blasting, dragline, front-end loaders, hoists, or other means.

Once the ore is out of the mine, the goal is to get rid of as much of the gangue (nonmetallic material) as possible and to concentrate the metal values for easy extraction at a minimum of cost and headaches.

There are many different kinds of tools used to extract metals, and new ones are invented daily. There are grinders, crushers, washers, separators, concentrators, classifiers, dredges, gold wheels, and centrifugal apparatuses, some water powered, some air powered. I will cover some of the standard equipment and their purposes.

Some equipment can be used in both primary and secondary extraction and refining. Most hard-rock mining is undertaken only by large, well-heeled operators. A case in point is the extraction and refining of gold from tellurides and quartz-bearing gold deposits. The recovery of free gold and platinum from placer gravels, from black sands in creeks, streams, and gravel beads, and from dry stream beds, on the other hand, is an operation that can be run by small operators with limited amounts of cash and equipment. In fact, anyone with a $8.98 gold pan and a little resolve can tackle black sands.

The basic difference between primary and secondary recovery and refining is quite simply one of volume. If you have a placer operation collecting ore containing one to two ounces of free gold per ton, you will have to work your way through a ton of gangue to recover your one to two ounces of gold, even at a 100% recovery rate, which is not likely. In contrast, if you are working with a pile of sterling silver or gold scrap jewelry, you have a relatively high concentration of metal values per unit weight of total material you must handle and process. Therefore, with secondary extraction and refining, you can spend a lot more time and money on the refining operation and still show a profit. Both secondary and primary processes, however, have a point of diminishing returns when costs are rated against percent values being produced.

Metal-bearing areas can belong to any of a number of chemical groups, including oxides, sulfides, oxysalts, and arsenides. The suffix "-ide" denotes a binary compound of two elements or radicals. For example, tin oxide (SnO_2) is a binary compound of tin and oxygen at one tin atom to every two oxygens.

Metal values are commonly found in the form of oxides. Examples are iron ore (Fe_3O_4), tin oxide (SnO_2), and lead monoxide or litharge (PbO).

Sulphides are binary compounds, one of whose two elements is sulphur. They are often subjected to oxidation during the refining process. This turns the value from a sulphide into an oxide. To oxidize means to add oxygen, combine with oxygen, or remove hydrogen. Rust is iron oxide (Fe_2O_3).

Ores whose metallic or mineral values are secondary sulphides and carbonates are known as oxysalts. An example is silver carbonate (Ag_2CO_3). A carbonate is a metallic or organic compound formed with carbonic acid (H_2CO_3). Carbonic acid is produced in nature by the reaction of carbon dioxide with water.

The metallic values in some more complex minerals are combined with arsenic to form natural binary arsenides. Examples of minerals containing arsenides are silver austinite (Ag_3AsO_3) and arsenopyrite or mispickel (FeAsS), which is a natural sulphide of iron and arsenic. These arsenides are extremely toxic. Arsenides of sulphur–arsenic combination are sometimes found with lead, nickel, copper, or cobalt ores. Sperrylite ($PtAs_2$) is a platinum arsenide often found in association with nickel sulphide ores. Sperrylite is considered a rare ore; it is found in Wyoming and Ontario, Canada. The only other known platinum ore is cooperite (PtS), a platinum sulphide.

The first step with any ore discovery is to determine ("prove out") the values the ore contains, in order to determine if it is economically feasible to set up and operate. This is a long and complicated process, subject to extreme market fluctuations; it should always be undertaken very carefully.

Because equipment and methods of extractive metallurgy vary depending on the type of ore body, the value present, and its richness, this book will give a general outline of how some ores are handled and treated; it will, however, provide detailed coverage of processes that are within reach of the small operator, such as the extraction and refining of free gold and platinum values from black sands.

The excavation of ore can take a form as simple as surface strip mining, when deposits lie directly below a fairly thin belt of overburden. The mining can be done with steam shovels, draglines, or front-end loaders.

In gold-bearing sedimentary deposits, placers, and dry river beds, some form of dredging will do the job—the simplest forms being the gold pan and the shovel. As with most ores (the exceptions include rich iron ore and bauxite—Al_2O_3), you are first going to have to concentrate the values, getting rid of as much of the gangue as possible at the lowest cost.

This is relatively simple with sedimentary deposits. However, if the values are trapped in quartz—as they are at Cripple Creek, Colorado, in underground gold-bearing quartz mines—or in one of the various tellurides, it is a different story.

Tellurides

The tellurides form a family of binary compounds of the element tellurium (Te) and another element or group. Five tellurides are particularly significant as sources of precious metals.

Altaite is a telluride of lead-carrying gold in various amounts.

Calaverite ($AuTe_2$) is a telluride of gold in which silver also commonly occurs. A high-grade calaverite can assay above 40% gold and above 3% silver, with the remainder tellurium. This is the king of tellurides.

Sylvanite [$(Au,Ag)Te_2$] is another gold–silver telluride; it can assay above 20% gold and above 13% silver.

Petzite is a silver–gold telluride in which the silver content usually exceeds the gold by a 2-to-1 ratio.

Hessite (Ag_2Te) is a simple telluride of silver which can be over 63% silver. It closely resembles petaite; both have a steely gray to black color. The streak test shows an iron-like black. Under the blow pipe, when mixed with a little carbonate of soda and subjected to a reducing flame on the charcoal block, the tellurium vaporizes and the silver and gold reduce to metallic silver–gold beads.

Tellurides are easily identified under the blow pipe or by means of a simple wet chemical test. If a material is suspected of being a telluride, a small sample should be ground up and dampened with water to make a small flat cake (no flux need be added). On the charcoal block, tellurium melts easily, volatilizing in fumes and coating the charcoal block with tellurous acid a short distance from the sample. When the sample is subjected to an oxidizing flame, the charcoal block's coating is white, with a red to dark yellow border. Under the reducing flame, the border disappears in a green flame. If selenium is present, the flame is bluish green. See Figure 1.4.

In order to identify tellurides using chemicals, first grind up a piece of the ore about the size of a navy bean, place this in a dry test tube, and add enough strong sulphuric acid with a dropper to cover the sample. If a telluride is present, a reddish violet color will show. The addition of sulphuric acid causes an exothermic reaction (produces heat). Let this cool and then add distilled water to the test sample, drop by drop, until the color disappears; finally, add a few drops of distilled water in excess. A grayish black sediment will precipitate (fall down). This is tellurium.

Other Gold-Bearing Ores

Other gold-bearing ores are quartz in dacite, schist, breccia granite, schist near granite and gneiss, quartz in slate near its contact with diorite, and quartz between slate and diorite. Gneiss is a banded or foliated granite-type rock in which mineral values can be found in layers. Diorite is a common country rock of the granite family, basically composed of hornblende and feldspar. Gold or other values can also be extracted from eruptives (igneous rocks produced by volcanic action,

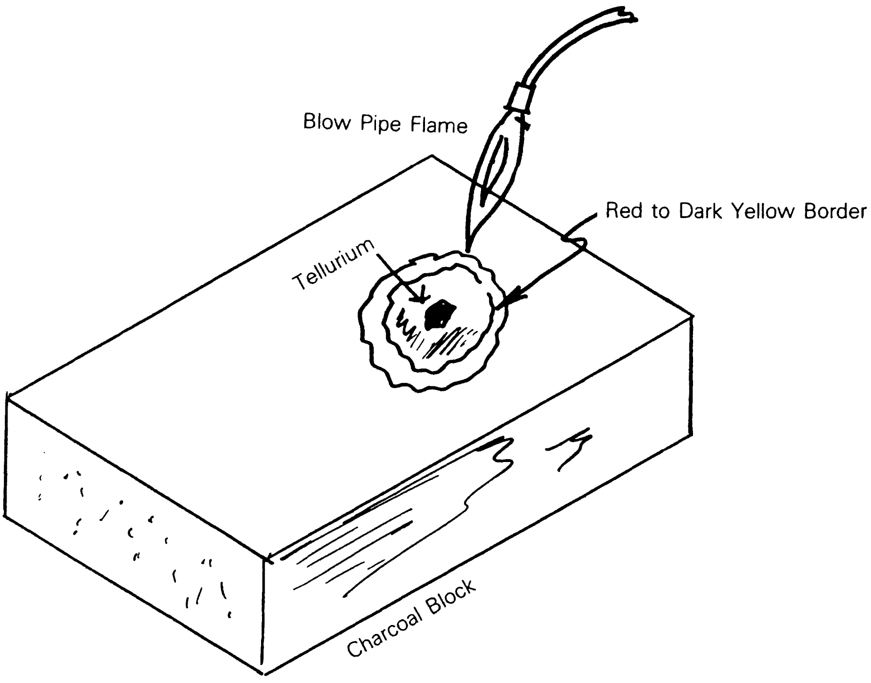


Figure 1.4. Tellurium under the blow pipe

past or present, such as andesite, basalt, dacite, latite, rhyolite, and trachyte), quartzite, sandstone, granite, jasper, limestone, serpentine, and slate.

Type of Country Rock and Possible Values

Rock: Schist and Gneiss

Possible Values

Cobalt (Co)
Copper (Cu)
Corundum (Al_2O_3)
Cryolite (Na_3AlF_6)
Gold (Au)
Graphite (C)
Iron Pyrite (FeS_2)
Lead, Silver, and Zinc (combined) (Pb–Ag–Zn)
Mercury (Hg)
Mica (a silicate)
Monazite (a rare-earth phosphate)
Nickel (Ni)
Quartz (SiO_2)
Silver (Ag)
Talc (Hydrous Magnesium Silicate)
Tantalum (Ta)
Tin (Sn)

Rock: Diorite

Possible Values

Gold (Au)

Rock: Eruptives *Possible Values*

Copper (Cu)
Fluorspar (CaF_2)
Gold (Au)
Iron (Fe)
Nickel (N)
Silver (Ag)

Rock: Quartzite *Possible Values*

Gold (Au)
Iron (Fe)
Lead (Pb)
Manganese (Mn)
Zinc and Lead (combined) (Zn–Pb)

Rock: Sandstone *Possible Values*

Antimony (Sb)
Barite ($BaSO_4$)
Carnotite ($V_2O_5 \cdot 2U_2O_3 \cdot K_2O \cdot 3H_2O$)
Coal (C)
Copper (Cu)
Manganese (Mn)
Mercury (Hg)
Oil Shale
Petroleum
Rock Salt (NaCl)
Silver (Ag)
Turquoise ($CuAl_6$)
Vanadium (V)

Rock: Granite *Possible Values*

Antimony (Sb)
Bismuth (Bi)
Copper (Cu)
Diamond (C)
Feldspar (an aluminosilicate)
Garnet (a trisilicate)
Gold (Au)
Lead (Pb)
Mica (a silicate)
Molybdenum (Mo)
Tantalum (Ta)
Tin (Sn)
Topaz (a flurosilicate)
Tourmaline (a borosilicate)
Tungsten (W)

Rock: Jasper *Possible Values*

Copper (Cu)
Manganese (Mn)

Rock: Limestone *Possible Values*

Antimony (Sb)
Arsenic (As)
Barite ($BaSO_4$)
Calcite ($CaCO_3$)
Cobalt (Co)
Copper (Cu)
Emerald ($BeO \cdot Al_2O_3$)
Flint (quartz)
Garnet (a trisilicate)
Gold (Au)
Lead (Pb)
Manganese (Mn)
Mercury (Hg)
Opal (SiO_2)
Sulphur (S)
Zinc and Lead (combined) (Zn–Pb)

Rock: Serpentine

Possible Values

Asbestos (Chrysotile)
Chromite ($Fe_3Cr_2O_3$)
Diamond (C)
Magnesite ($MgCO_3$)
Mercury (Hg)
Nickel (Ni)
Platinum (Pt)
Talc (Hydrous Magnesium Silicate)

Rock: Slate

Possible Values

Arsenic (As)
Coal (C)
Gold (Au)
Lead (Pb)
Lead and Zinc (combined) (Pb–Zn)

Equipment and Procedures

Crushing and Grinding

In order to free mineral values trapped in rock-type ore, you must, after getting the ore out of the ground, crush it. The first crushing is called primary crushing. A wide variety of machines are sold for this purpose, and several types are very common.

The jaw crusher consists of a fixed plate and a moveable plate serving respectively as the fixed jaw and the working jaw of the machine. The idea is to squeeze the ore with enough force to fracture it. As the ore breaks into smaller units, it falls down into the progressively smaller space between the jaws. The action is repeated in this manner until the material is small enough to fall through the discharge end. The adjustable discharge gap is set to the desired maximum size you wish the material to be after primary crushing. The moveable jaw is actuated by a crank or throw from a fly wheel, which operates the toggle knuckle, moving the jaw in and out. In essence, it is simply a progressive nutcracker. The size of the rock that can enter the feed end of the jaws is controlled by a heavy screen, called a "grizzly," whose mesh is of the desired diameter. See Figure 1.5.

The cone crusher is very similar to an old-fashioned hand-cranked coffee grinder, only it is horizontal. See Figure 1.6. The gyratory crusher is similar in action to the cone crusher. Both operate on the principle of gyratory action, alternately reducing and widening the space between the gap and the set to produce a circulating action. See Figure 1.7. The physical action of the cone crusher and of the gyratory crusher on the ore ("burden") is exactly the same as that of the jaw crusher. It is a squeezing force causing the burden to fracture and splinter.

The hammer mill, as the name strongly suggests, uses a striking action—the hammers repeatedly strike the material in a rotary flailing action. As a result, the material is crushed by the repeated blows, by internal collisions, and by

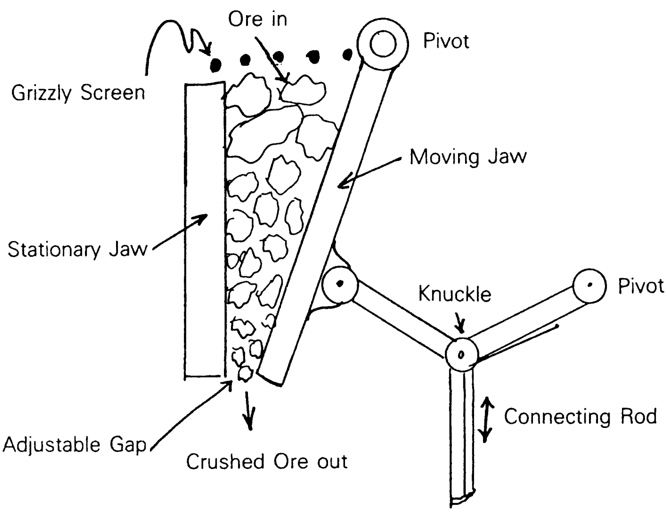


Figure 1.5. Basic jaw crusher

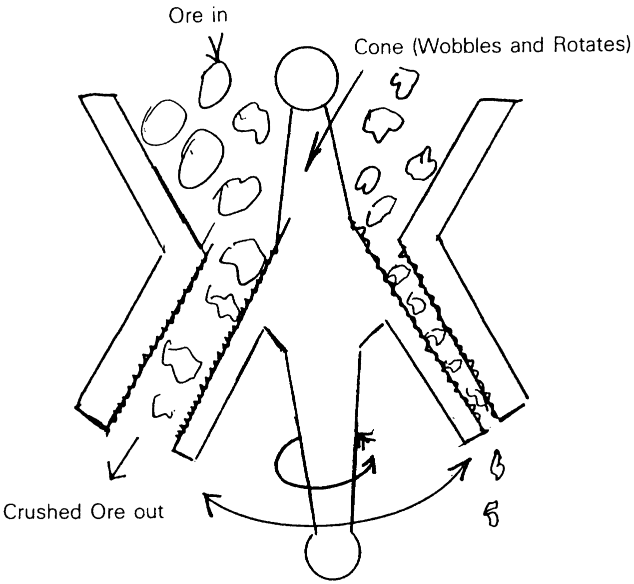


Figure 1.6. Basic cone crusher

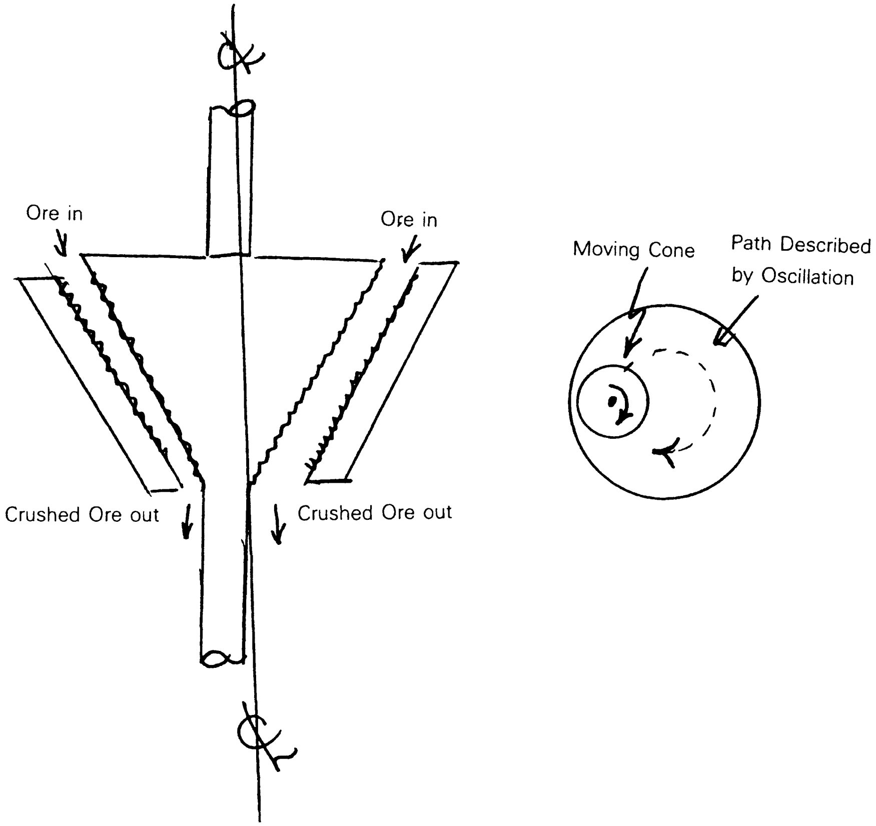


Figure 1.7. Inverted cone crusher

collisions between the material and the walls of the case. See Figure 1.8. The hammer mill is usually relegated to crushing fragile, easily splintered material, such as coal or fluorspar.

A roll crusher uses both squeezing and striking actions. The rolls are faced with teeth, which provide some striking action and also carry or force the material between the rolls, where the material is subjected to a squeezing force.

Jaw and gyratory units are usually classified as primary crushers. The jaw crusher usually handles larger material, with the output of the jaw crusher being fed to the gyratory unit.

Generally, a primary crusher reduces the ore to a size at which it can be handled by another unit—a secondary crusher—which further reduces it. After this, the ore is subjected to grinding, to reduce its size even more. This is accomplished in a ball or rod mill.

A ball mill is a simple device. Crushed ore is ground fine (powdered) by being

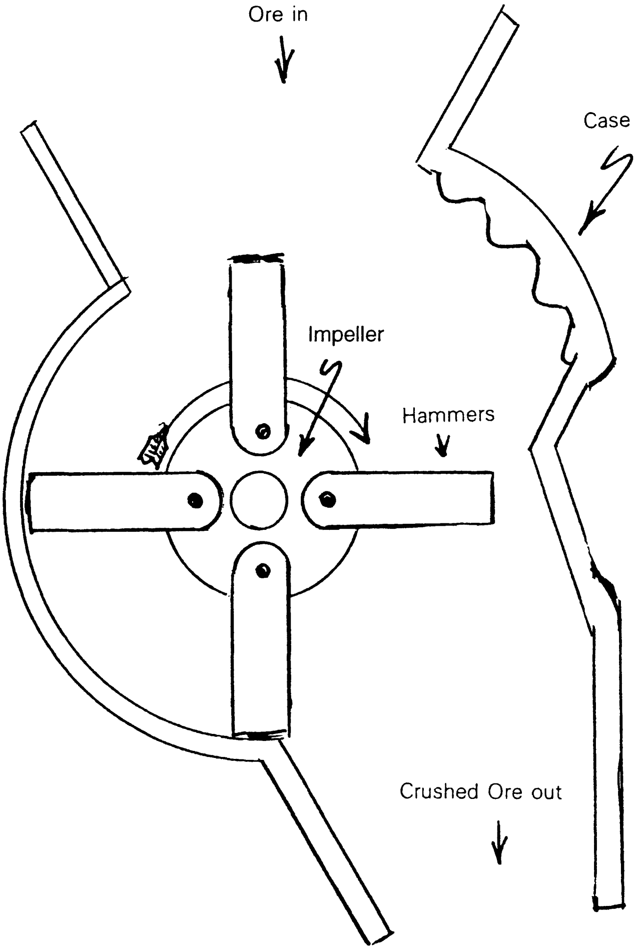


Figure 1.8. Basic hammer mill

rolled in a cylindrical drum (ball mill) that contains chilled iron or flint balls. A rod mill is similar in operation, with the exception that the balls are replaced by rods. See Figure 1.9. Grinding can be done wet (in water) or dry, depending on personal choice and the material being handled.

For years, finely divided gold trapped in such materials as quartz was worked in stamp mills. A stamp mill is in reality a simple cam-operated drop hammer. The hammer is raised by a cam and becomes free-falling when it runs off of the cam. The hammer pounds the crushed ore, which is then fed to the mortar. Next, the powdered material is discharged from the mortar across a series of mercury plates and mercury wells, where the gold and any silver in the material become amalgamated with the mercury on the plates and in the wells. See Figure 1.10.

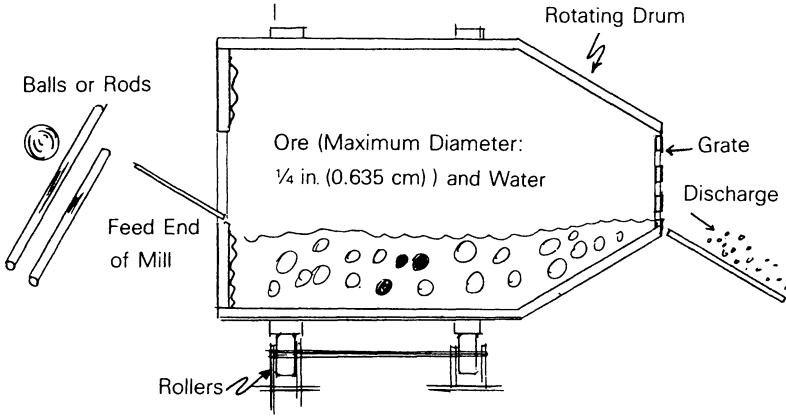


Figure 1.9. Rod or ball mill

All this crushing and grinding is for one purpose: to obtain the release of entrapped or encapsulated metallic values, whether they are in a free metallic state or in the form of an oxide, a sulphide, an oxysalt, or what have you. In testing, samples can be ground in a simple steel or cast-iron mortar with a pestle. See Figure 1.11.

The products of crushing and grinding operations are, in some cases, recycled through various operations; in other cases, the oversized material that slipped

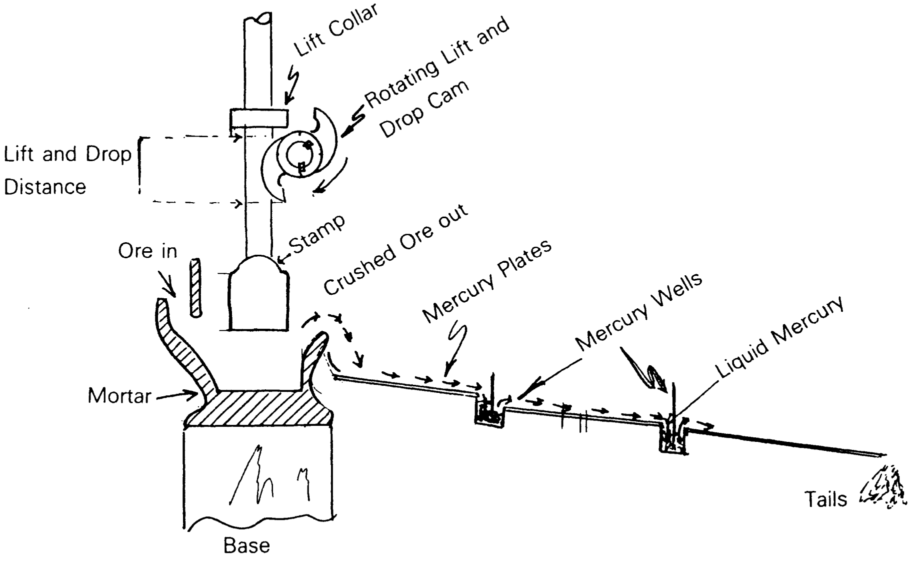


Figure 1.10. Stamp mill, plates, and wells

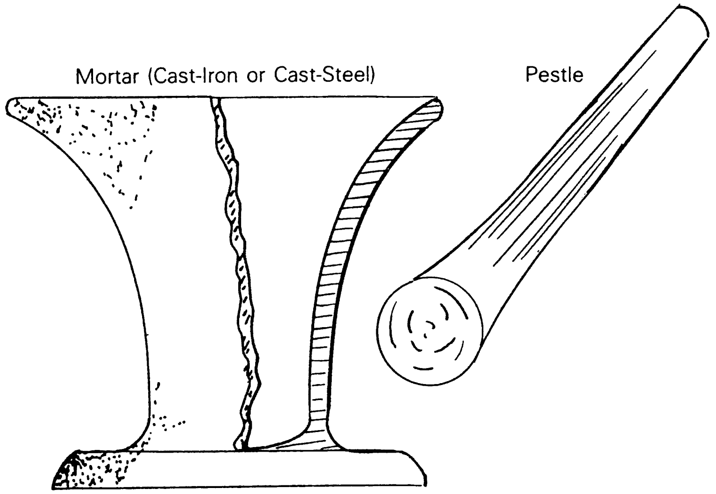


Figure 1.11. Mortar and pestle

through is separated by screening in rotary screens, called "trommels." The material that is too large is either discarded or rerouted for regrinding. See Figure 1.12.

Decrepitation

Some ores can be broken apart by the process of decrepitation. If you have a combination of a crystalline material and an amorphous material or of two crystalline materials that you can roast to the crackling or shattering point (decrepitate) at different temperatures, and you heat them to the lower of the two decrepitation temperatures, you can create a condition in which separation is simple. Take, for example, an ore of zinc sulphate ($ZnSO_4$) in combination with barite ($BaSO_4$). When heated, the crystalline zinc sulphate will decrepitate into fine particles while the barite remains solid, making separation a simple screening operation.

This method can also be used to separate small particles of gold trapped or encapsulated in small quartz particles. If heated sufficiently on a steel plate or under a blow pipe, the quartz will decrepitate, freeing the values. Decrepitation is caused by the expansion of the chemically combined water of hydration in the crystals as it vaporizes.

Concentration

The next step is a final separating or concentrating operation. The object is to free the values from any remaining gangue.

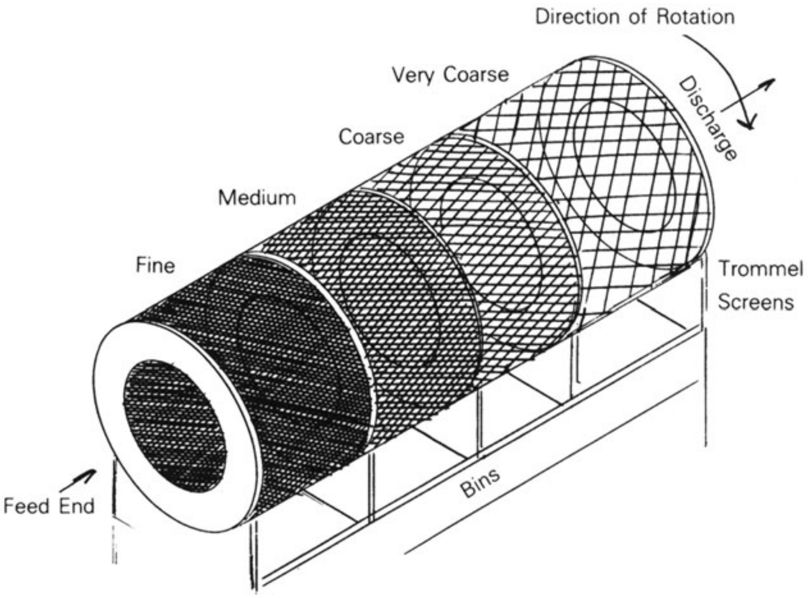


Figure 1.12. Basic trommel

In secondary separation, unwanted material is not commonly called gangue because it frequently has value itself—but relative to the more precious material being isolated, that is what it is. For example, if you have a piece of sterling silver (which is an alloy of copper and silver) and you want to free the silver, the copper becomes the gangue. In most cases, the final separation or concentration is not entirely pure but is sufficient to make the next step—that of reduction or refining—possible.

Separation and concentration operations, whether wet or dry, are usually based on the difference in specific gravity of the value versus the gangue. Magnetic material can be separated by magnetic separators. The two simplest methods of concentrating values based on differences in specific gravity are panning gold and working dry placers or river beds with a blanket.

Gold has a specific gravity of 19.32; silica (as quartz), a specific gravity of 2.65; black sand magnetite (Fe_3O_4), a specific gravity of 5.18; and flint, a specific gravity of 2.6. Gold is therefore 7.29 times heavier than quartz or flint and 3.73 times heavier than magnetite. If a mixture of these four materials is panned correctly, the gold, being heavier, will stay behind as first the materials with a 2.6 specific gravity and then the black sands are floated off.

A common practice with old-timers was to place roughly equal-sized material, as determined by a sieve, on a blanket and then pop it up into the air, letting the wind take off the light materials in exactly the same manner as chaff used to be

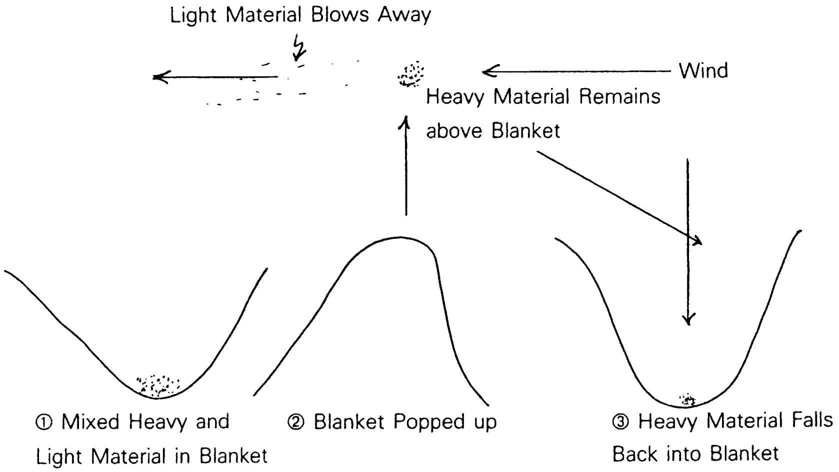


Figure 1.13. Blanket concentration

winnowed from grain. Further concentration was accomplished by spreading out the gold and blowing lightly over it, orally or with a bellows. See Figure 1.13.

The dry sluice apparatus consists of a sluice with wooden riffles on a porous canvas deck. As the material makes its way downward, the mechanism that shakes the sluice also operates a bellows from below, which puffs intermittent blasts of air up through the canvas to the material. These blasts of air carry away the light material. Some bellows are single stage (puffers), whereas others are double-stage and supply a continuous current of air. There are innumerable types of final-stage classifiers and concentrators.

Elutriation

Elutriation is the washing, separating, or sizing of fine particles of different weights by suspending them in a current of air or liquid—usually water. Some elutriating devices are the gold pan, the sluice, the rocker, the rug sluice, the gold spiral wheel, the spiral trommel, the Humphrey's Spiral, the jig, the vortex cyclone, the vertical flow trap, and the log washer.

To use a gold pan (Figure 1.14), fill the pan with gravel and place the pan

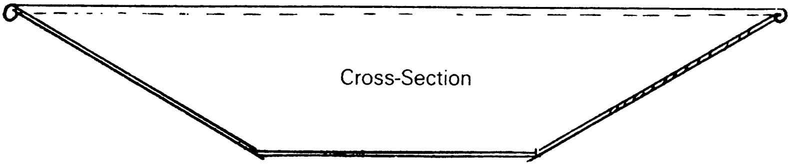


Figure 1.14. The gold pan

and its contents under water (the stream). The initial washing is done by stirring the contents by hand to break up the lumps and get everything wet. As the water in the pan becomes muddy, replace it with fresh water. After the initial washing, remove all the large pebbles and stones that are obviously gangue. Holding the pan under water, do the initial classification by simultaneously shaking the pan back and forth and oscillating it in a circular pattern, reversing the direction of the motion from time to time. This allows the heavy particles (such as black sands, gold, and platinum particles) to settle to the bottom.

The next step is to wash away the light gangue. Raise the pan out of the water, and dip the lip of the pan into the water at an angle of about 30°; then quickly withdraw the lip from the water. The resulting reverse wave washes light material, which is in suspension, out over the lip, exactly as waves receding from a beach carry sand back with them, leaving shells and larger stones uncovered. By striking the pan on the side from time to time (to keep the heavy material on the bottom) and by repeating the lip-washing action, a small amount of material consisting of heavy sands and the precious metal values, if any are present, should remain.

At this point, wash the remaining material into another pan, or a suitable plastic or metal receptacle, to dry. Trying for a complete separation by panning usually results in a loss of considerable amount of the values. Fine flat and small particles will, if worked in muddy water, float out over the lip. The pan must be completely grease-free because any fine values that become coated with oil will be lost to floating. See Figure 1.15.

The gold pan is easy to master with practice and is also used in secondary refining for various other purposes. The dried material can be further separated by using a blow box and a small permanent magnet. Remove obvious large values (small nuggets and so forth) with tweezers. Then remove the magnetic material with a small permanent magnet. See Figure 1.16.

The material is spread out evenly in the blow box and, by tapping the box and blowing across the material, the lighter gangue can be swept off. With practice, a remarkable separation (concentration) can be obtained.

A bater is a wooden-type gold pan, shaped like a bowl. It is operated while practically submerged, using a circular, oscillating motion. It is said to be superior to the conventional steel pan. See Figure 1.17.

A sluice is a trough with riffles in its bottom. Material is first relieved of large

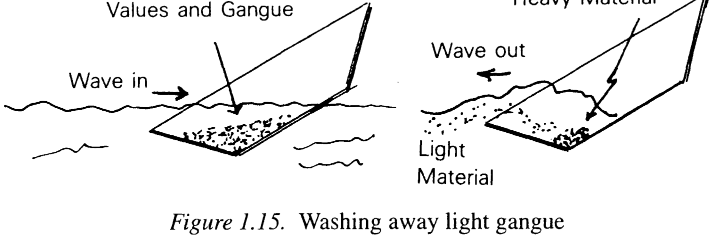


Figure 1.15. Washing away light gangue

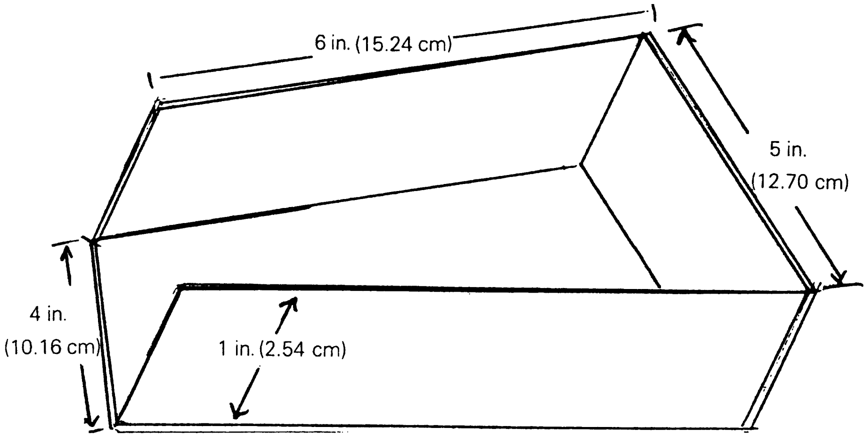


Figure 1.16. The blow box

material by a heavy screen, called a grizzly. The remaining material is then washed down the inclined sluice, with the heavier parts of it settling (or becoming trapped) behind the riffles. The light material continues down the sluice and goes over the end. See Figure 1.18.

A rocker is simply a sluice that can be rocked from side to side as the material travels down it. The sloshing of the material from side to side on its downward trip gives some gold pan action, effecting a better settling of the heavy material by its action. Rocking also effectively extends the surface area of the sluice and the length of time the material is retained on its downward trip. See Figure 1.19.

In some sluice boxes and rockers, the bottom is covered with a rug or mat—the idea being that the small, fine particles will become ensnared or trapped in

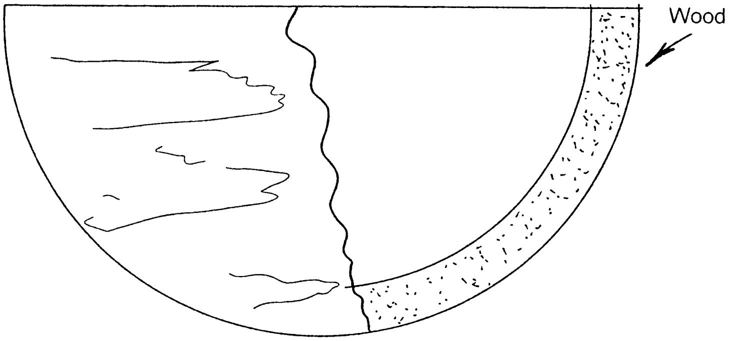


Figure 1.17. The bater

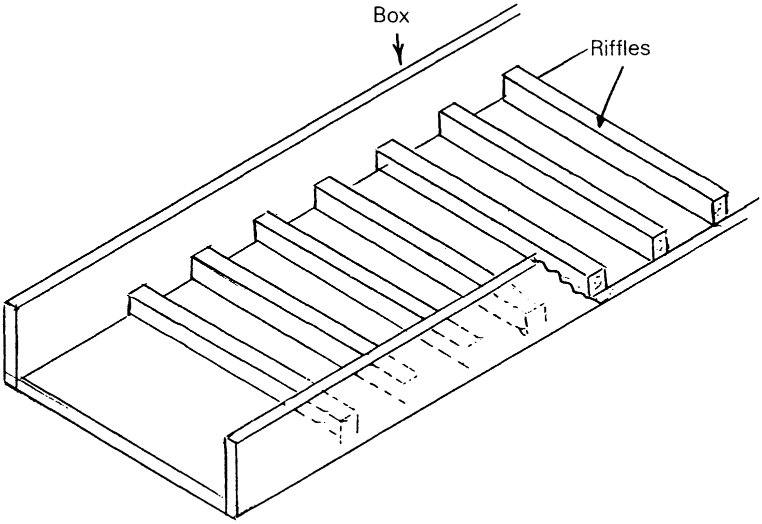


Figure 1.18. The basic sluice box

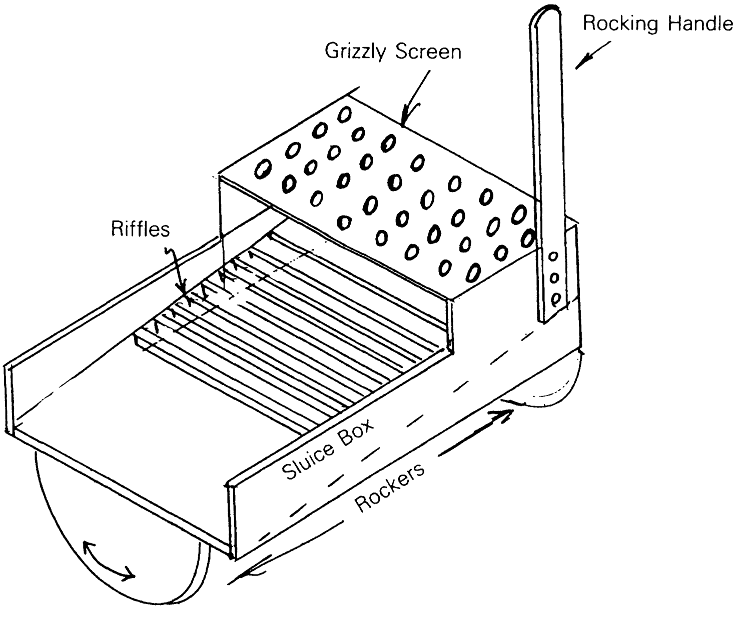


Figure 1.19. The rocker

the fibers. In some cases, the sluice's riffles are simply holes punched through a steel plate that is bolted down to the rug; in others, the rug-covered trough consists of expanded wire mesh. See Figure 1.20.

Another device for separating heavy particles from light is an inclined wheel that has on its face a spiral groove (molded or machine cut). The inner end of the groove terminates at a central opening. The wheel is rotated, producing a spiraling ramp that conveys material introduced at the bottom of the wheel upward in the groove. Water spray is played on the revolving wheel, causing a downward flow of wash water that carries light material out of the grooves during its upward journey. The heavy material, because of its specific gravity, hangs in the groove and is discharged at the central opening. The tumbling action of the material during its ascent keeps exposing the lighter gangue to the action of the wash water flowing downward. The material is circulated to the wheel until no further color can be seen climbing the wheel. The wheel's angle of inclination is adjustable, as is the water flow.

The Dam machine is a simple device that relies on both elutriation and centrifugal force, much as a cream separator does. It consists of a circular pan equipped with an inner discharge spout, through which the lighter gangue flows. Water under pressure is delivered to the pan through a water inlet fixed at a tangent to the pan. The water delivery is adjusted so that the crest of the water in the pan, which is traveling in a circular motion, is maintained close to the top of the pan's edge. Because the central discharge is lower than the pan's edge, the spiraling water forms a vortex discharging through the top of the central outlet.

When the material to be concentrated or relieved of its gangue is fed in (dribbled) at the top outer edge of the pan, the swirling water causes a centrifugal separation of light material from heavy material. The light material is then drained away through the central discharge. Like most other elutriators, a Dam machine

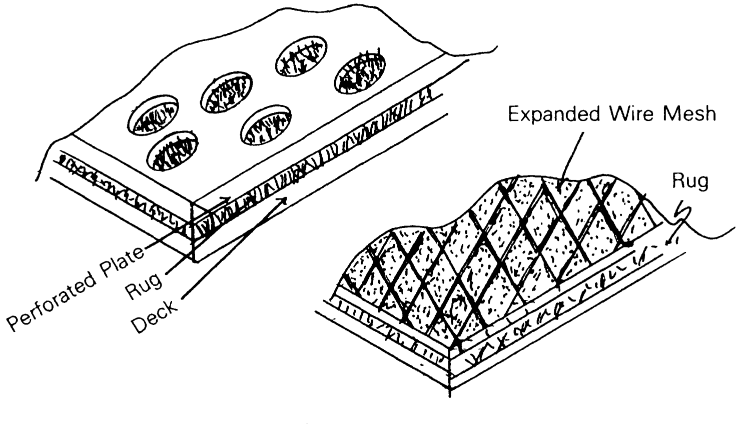


Figure 1.20. The rug bottom sluice

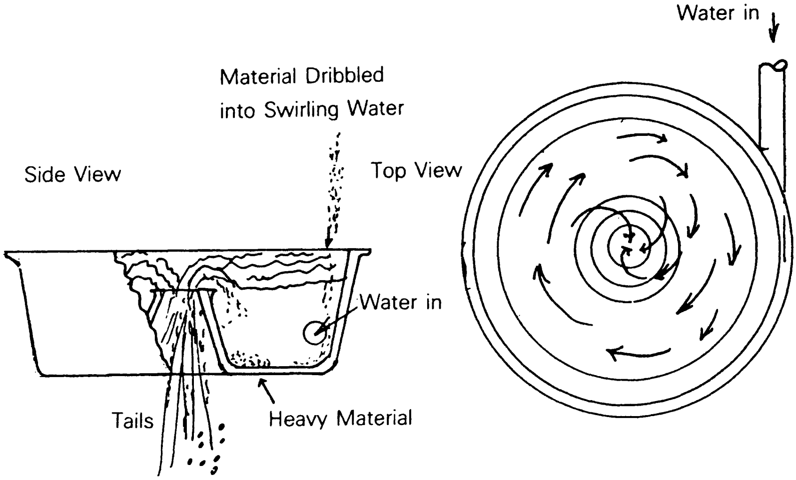


Figure 1.21. Centrifugal separation in the Dam machine

will not make a complete separation, and the concentrated material must be treated by other means (such as mercury recovery or chemical recovery) for complete separation. See Figure 1.21.

Inclined tube classifiers operate on the principle that when a liquid is running up an inclined tube, the fluid on the top of the tube runs faster than the fluid on the bottom. When material is introduced into this stream (with the flow velocity adjusted correctly for the material to be separated), the light material will travel upward and out of the tube, and the heavier material will go downward along the bottom of the tube. See Figure 1.22.

There are log washers, all sorts of uphill and downhill spiral washers, jigs, vertical spiral washers, vortex cyclones (named after the cyclone dust arrester), flow traps, and tables. Some jerk, some jump, some vibrate, some stand still, and some gyrate and jump. They may be operated by air, by water, or by a combination of the two. In some, the gangue is delivered upward and the values downward; in others, the directions are reversed. Their usefulness, too, can vary greatly.

Flotation

Flotation equipment differs in both design and operation from other types of equipment. It is widely used and can be very effective, once it is understood.

The original use of the flotation method was to concentrate sulphide minerals, as early as 1904. Today, with additives and with specialized alterations in the physical arrangement of the cells, flotation is used for a wide variety of material separations.

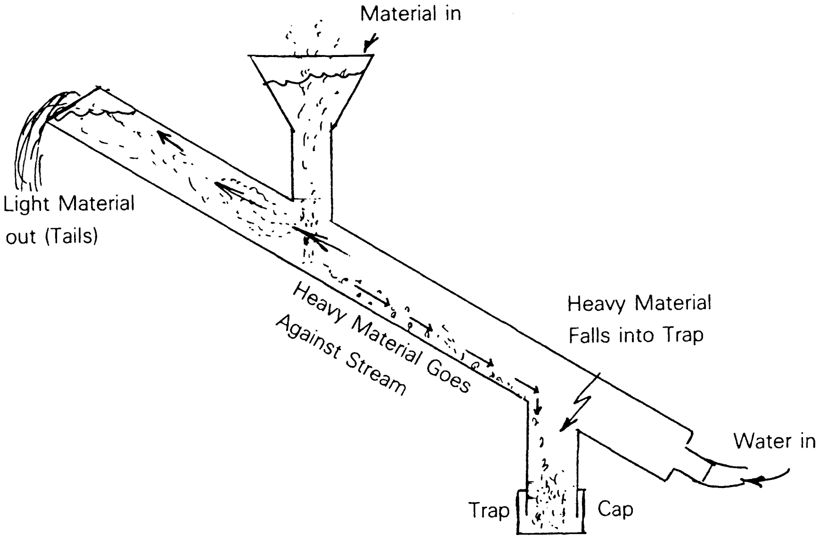


Figure 1.22. Inclined tube classifier

Simply put, selective flotation is accomplished by adding the proper reagents to a mixture of ground ore and water, which is kept agitated with paddles or propellers (impellers) while air is bubbled through it. This causes a frothing action. If you have added the correct reagents for the mineral you want to collect, the particles of that mineral will attach themselves to the froth bubbles and come to the surface, where they will form a froth concentrate and then be skimmed off. The unwanted gangue remains on the bottom of the cell; reagents called depressants are added to prevent the gangue from getting into the froth or coagulating in the cell.

By changing the reagent, you can perform more than one kind of separation. This is useful when the mixture has two or more values in it. Even when finely ground, an ore can give a high rate of recovery through the flotation process when other, more conventional methods would involve excessive losses (known as high slime losses) due to the fineness of the grind.

Some ores require more than one round of concentrating. In this case, the concentrate from one cell is reconcentrated in the next cell. The gangue may also be transferred to another cell by further concentration or for the concentration or recovery of a different material requiring different reagents.

Froth flotation is actually a chemical sorting operation based on ion exchanges, ionic conditions at the solid interface, contact angles at the interface, and surface tension. It can be used, with the proper reagents, soaps, and wetting agents, to distinguish not only a mineral from gangue but one mineral from another in the same cell. See Figure 1.23.

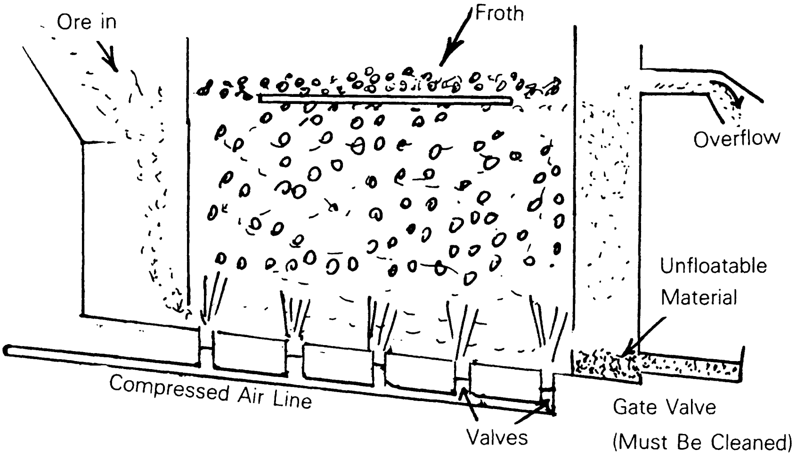


Figure 1.23. Simple flotation cell operated by compressed air

There is an old story that the flotation method was discovered by women washing miners' clothes in wash tubs, using scrub boards; they discovered that the froth or soap suds on top, when skimmed off, carried high concentrations of mineral values. This could very well be.

You can raise the specific gravity of a liquid by putting metallic ions into it. Any particles of a material that are placed in the solution will float or sink depending on whether their specific gravity is higher or lower than the liquid's. A human being, for example, sinks easily in distilled water but floats like a piece of wood in water whose salt content is high enough.

This is the basis for a lot of separations performed in the lab. If the specific gravities of two solutes (dissolved materials) are close to each other, you might have to use a centrifuge to get a separation. Water has a specific gravity of 1.0 and gasoline (on the average) a specific gravity of 0.75. Therefore, the gasoline will float on top of the water. A common inorganic material used for flotation separation is thallous malonate, a salt of the metal thallium (Tl). Thallium has a specific gravity of 11.85. Thallous malonate is dissolved in water to increase the liquid's specific gravity, and its amount is adjusted to give a float or sink value to the material to be separated. In industry, thallous malonate is used to recover diamond dust (powders) used in grinding and polishing operations. Diamond has a specific gravity of 3.521. See Figure 1.24.

Friction

Another method of separation used is based on the difference in friction between materials. One very simple but efficient apparatus I have seen in operation consists of a smooth rubber belt traveling uphill at a rather slow pace. As the belt travels

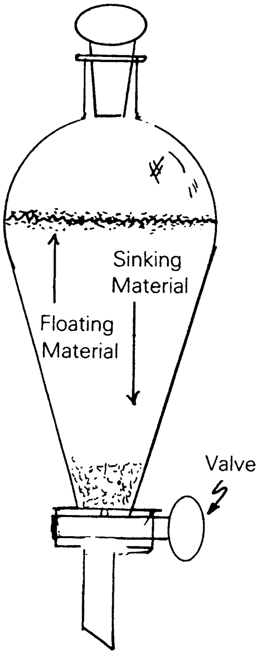


Figure 1.24. Separatory funnel

upward, the material (finely ground gold-bearing black sands) is sifted onto the belt about midway between top and bottom. At this point, a fine water spray is played on the belt, so that you have a downward flow of water as the material moves upward. The gangue washes down while the gold particles stick to the belt with great tenacity—especially when the gold appears in the form of flat particles (platelets).

Several advantages can be exploited by this operation: specific gravity differences, the shape of the materials, and their frictional differences. I purchased some extremely smooth white rubber belting from a food machinery manufacturer and built a simple unit using a hand-held water hose, which allowed me to vary the water's pressure, volume, and direction. The belt was driven by a gear-reducer motor with an autotransformer, giving me a range of speeds. I then loaded (salted) a known weight of fine gold into some barren, sharp silica sand of 100 mesh. To my surprise, I was able to recover 99.99% of my gold completely free of silica, so this appears to be a viable approach for some applications. See Figure 1.25.

Working with ores can be complex and confusing. It is imperative to your operating success that you never buy any mining machinery—concentrators, high graders, elutriators, or whatever—without a show-me deal with your material.

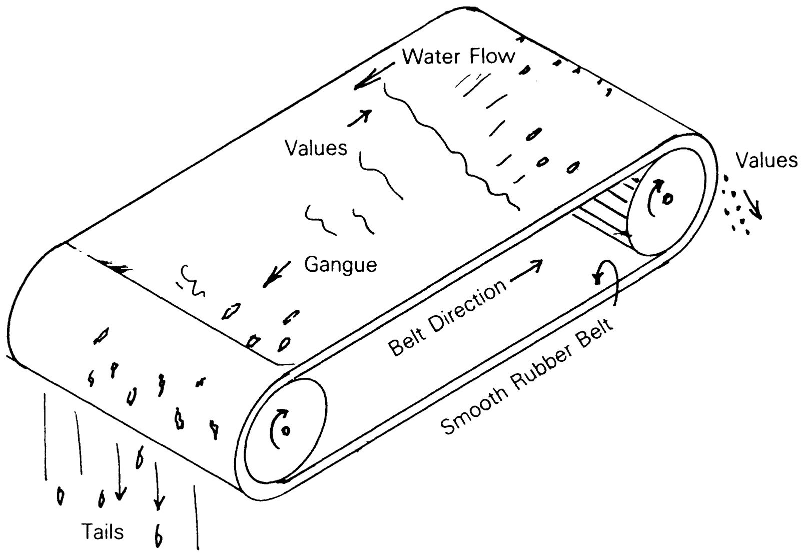


Figure 1.25. Moving wet belt separation

The big thing for placer gravel is small dredges. These are simply sluices with a suction pump to deliver the material to the head of the sluice. Dredges are rated by pump discharge size: those from 1 to 2 in. are called one-man dredges because they can be operated by one man; those from 3 to 4 in. require a two-man operation; and those above 4 in. require an even larger operating crew.

Avoid any complicated machine that is advertised to do it all. Some wet chemical and electrowinning ensembles are simply collections of unrelated equipment housed in fancy cabinets and sold with little instruction booklets for a very high price. Bought piece by piece in the marketplace, they are considerably less expensive.

Trading in Metals

In many cases it is one thing to recover precious metals and another thing to market them. Of course, you want your fair price.

This field is quite complicated and is called the trading triangle. You are dealing with many areas: physical movement of the material, ownership, and so forth.

From the producers side of the game:

Sells FOB—Sells CIF—Sells Delivered—Sells Warehouse

From the consumers side of the game:

Buys FOB—Buys CIF—Buys Delivered—Buys in warehouse.

It is a real zigzag confusing network requiring a great deal of know-how:

Buys CIF → Sells CIF → Buys FOB → Sells FOB →
Sells Delivered → Buys Warehouse → Sells Warehouse →

Intertwined in all this zigging and zagging there are brokers, producers, agents, and banks. I do not think you want to get into the game. Best to be a broker.

Common Terms Used in Metal Trading

One thing you should know is the terms that apply. Let us say that you concentrate a precious metal ore or placer claim via tabling, jigging, or whatever, and you are ready to deal directly with a smelter and refiner, a trader, or a broker (United States or abroad). It pays in big dividends if you are at least familiar with the jargon that is in common worldwide use today:

Ad valorem. According to the value.

A/F. Measured across the flat (square or hex).

Alloy. Combination of two or more metals.

Alluvial deposit. Earth, sand or gravel.

Aluminium. Variation of spelling of aluminum.

Antimony regulus. Metallic antimony.

Arbitrage. Buying futures while selling an equal amount to another market (a real tricky operation requiring both brains and guts).

A/sales. Account sales, the account of sales submitted by a seller, broker, and so forth.

Assay. Independent evaluation of ore, metal, secondary, primary, or mixed scrap, and so forth. The assay can and is usually made at various points from origin to market. An outturn assay is one taken after smelting or melting.

The **outturn assay** is quite common with scrap (i.e., electronic mixed bag scrap, sweeps, pan scrap, buffs, ore concentrates, tank house slimes, low grade scrap, and so forth. It is melted or smeltered, cast into ingots from which borings are taken and assayed by fire or wet chemical. This assay is the outturn assay.

At arms length. This expression signifies that the parties entering into a deal or transaction have no prior financial or other connection between them. It is a legal term used also in the trading world.

Base metals. Ferrous or nonferrous nonprecious metals (i.e., copper, zinc, lead, iron, etc.).

Basis price. (strike price). Price agreed on between seller and buyer.

Bid. Price at which the buyer wishes to buy.

B/L. Bill of lading.

Borrowing. Borrowing metal from the futures market.

BS. British standards.

By-product. Any metal recovered in small quantities from producing another metal (that is, gold from copper refining, etc.).

Carrying. Borrowing and lending on the LME (London Metal Exchange).

C & F. Cost of freight.

CIF. Cost of insurance and freight.

Cobbled ore. Ore which has been usually sorted by hand, lump by lump.

Comex. New York Commodity Exchange, often meaning the price or gold or silver, spot price New York (that is, gold Comex $395.00 troy/oz.).

Concentrates. The first step in upgrading an ore from low levels of value upward.

Cryogenics. Freezing large massive oversize chunks of metal or plastic covered scrap to a low temperature, thus embrittling it.

Custom smelter. One who smelts ore for independent mines for a percentage or fee.

Deduction. A deduction on the payment on concentrates to cover the smelter's unavoidable value losses in smelting.

Draw back. Refund on duty on re-export.

Ex warehouse. The seller must load buyer's truck.

Fire refining. Refining in a reverberatory or rotary furnace.

F.R. Fire refined.

Freight forward. Freight to be paid by consignee.

Gangue. Nonmetallic material in the ore.

G.F.D. An order to buy that is good only for a day. If not acted upon that day, it is automatically canceled.

Prompt date. The date metal must be delivered as per contract date.

This is just a short list to let you know how complex it could get.

Ship to Overseas Refiners

It is becoming more and more the practice of mining companies both large and small to just engage in concentrating real tight, drumming the high-grade cons, and shipping to an overseas smelter and refiner. The basic reason for this is in order to smelt one's own material today, there is an enormous capital dollar outlay. A great deal of this outlay is for nonproductive equipment (that is, bag houses, scrubbers, water purification, toxic waste disposal, etc.) all of which cost to operate and maintain. This cost added to operating cost does not put you in a very competitive position, plus you must satisfy countless regulatory agencies (EPA, OSHA, etc., etc.). Slip up and you get fined out of business.

It would be a lot simpler if these agencies would tell you which equipment to buy or install that would comply with the various rules, regulations, and so forth. However, this is not the case. The procedure is this: You submit plans, specifications, and so on to the agency or agencies involved. These agencies review all this and give you the go ahead. You get everything up ready to go, then they come out and tell you that it does not comply. You start over. No one, not even the manufacturers of pollution control equipment, will guarantee that if you follow certain procedures, you will comply. Now couple this with the fact that you can comply today and shortly down the line, the regulatory agencies change the rules. You start over. If you are involved in the recovery of primary precious metals (that is, placer, ore), you can even on a small or medium size operation go this route. Concentrate, concentrate, drum, and ship overseas. That is the best way to go.

Refiners, Smelters, Brokers, Traders, Assayers

The question I have been asked many, many times is where can I find a buyer for my cons, gold and platinum bars, sweeps, buffs, ash, dore, photographic film, residues, and so forth? Well, it is all in one paperback book, which is a must for everyone involved in the precious metals game: *Precious Metals Data Book* published by Metal Bulletin Books Ltd., Surrey, U.K. In its 253 pages are listed smelters, refiners, brokers, and mining companies worldwide, with complete, detailed information: head office, location, phone, fax, telex; management (executive director, sales, etc.); date established; capital; number of employees; ownership; subsidiaries; associates; works, smelter, refinery, and so on; products; brands and analysis; sales offices; buyers (and what they buy).

2

Chemistry

There are several basic chemical reactions you should understand in order to follow the discussions of more complex extractive methods and refining operations. This book will deal with all types of reaction and change, involving oxidations, reductions, ionizations, solubilities, precipitations, crystallizations, vaporizations, bulk and atomic weights, and conversions.

It is foolhardy and dangerous to go about any type of chemical extractive or refining procedure without knowing exactly what is going to happen, why it is going to happen, and how. If you proceed by the "let's see" method of chemical operations, you may find yourself involved in what is called high-speed chemistry, accidentally producing a violent explosive reaction or a deadly toxic gas or compound.

Many silver, gold, and mercury compounds are highly explosive fulminates, and many reactions are toxic—some extremely so. Hydrogen cyanide or hydrocyanic acid (HCN), for example, which is formed by adding an acid to a cyanide, is highly toxic by ingestion, inhalation, or through the skin. It is the gas used to execute people in the gas chamber.

Some metal compounds, such as silver nitrate and silver chloride, are toxic; some metals themselves are toxic, such as thallium and mercury. Mercury fumes are toxic, and so are mercury compounds that can be absorbed through the skin or inhaled. Some chemicals are extremely toxic in any form: as a compound, in solution, or as a gas. I will point out the particular dangers associated with each test or operation I describe in this book.

The point I am trying to make here is that it is essential for you to have a well-organized method and procedure to follow, and to know what to expect at each step. This applies to both qualitative and quantitative work. In the branch of chemistry you will be concerned with, the distinction between qualitative and quantitative work is often minimal or even nonexistent.

It will be helpful to you to learn to think and work in metric units (designated as SI units), which the international community has agreed should replace all other units of measure.

The Basic Seven Units

m = meter
kg = kilogram
s = second
A = ampere
K = kelvin
mol = mole
cd = candela

Derived Units

Hz = hertz
N = newton
J = joule
W = watt
C = coulomb
V = volt
F = farad
S = Siemens
Ω = ohm
Wb = weber
T = tesla
H = henry
lm = lumen
lx = lux
Pa = pascal

Some Conversion Factors

Length

1 centimeter	0.394 inches
1 inch	2.540 centimeters
1 meter	3.2808 feet
1 foot	0.305 meters
1 meter	1.0936 yards
1 yard	0.9144 meters
1 kilometer	0.62137 miles
1 mile	1.60935 kilometers

Area

1 square centimeter	0.1550 square inches
1 square inch	6.452 square centimeters
1 square meter	10.764 square feet
1 square foot	0.09290 square meters
1 square meter	1.1960 square yards
1 square yard	0.8361 square meters
1 square kilometer	0.3861 square miles
1 square mile	2.590 square kilometers
1 acre (U.S.)	4840 square yards

Volume

1 cubic centimeter	0.0610 cubic inches
1 cubic inch	16.3872 cubic centimeters

1 cubic meter	35.314 cubic feet
1 cubic foot	0.02832 cubic meters
1 cubic meter	1.3079 cubic yards
1 cubic yard	0.7646 cubic meters

Capacity

1 milliliter	0.03382 ounces (U.S. liquid)
1 ounce (U.S. liquid)	29.573 milliliters
1 milliliter	0.2705 drams (U.S. apothecaries)
1 dram (U.S. apothecaries)	3.6967 milliliters
1 liter	1.05671 quarts (U.S. liquid)
1 quart (U.S. liquid)	0.94633 liters
1 liter	0.26418 gallons (U.S. liquid)
1 gallon (U.S. liquid)	3.78533 liters

Mass

1 gram	15.4324 grains
1 grain	0.0648 grams
1 gram	0.03527 ounces (avoirdupois)
1 ounce (avoirdupois)	28.3495 grams
1 gram	0.03215 ounces (troy)
1 ounce (troy)	31.10348 grams
1 kilogram	2.20462 pounds (avoirdupois)
1 pound (avoirdupois)	0.45359 kilograms

Power

1 watt	0.73756 foot-pounds per second
1 foot-pound per second	1.35582 watts
1 watt	0.056884 Btus per minute
1 Btu per minute	17.580 watts
1 watt	0.001341 horsepower (U.S.)
1 horsepower (U.S.)	745.7 watts
1 watt	0.01433 kilogram-calories per minute
1 kilogram-calorie per minute	69.767 watts
1 watt	1×10^7 ergs per minute
1 lumen	0.001496 watts

I occasionally depart from the metric (SI) units, particularly with such things as nut and bolt sizes, because I am not completely metrified. In the lab, I often have to stop and convert.

Two things are indispensible aids to chemical work: a pocket calculator—the type that gives you not only basic operations, percentages, and square roots but also metric conversions—and a readable (preferably double-sided) periodic table of the elements.

Matter

Matter is defined as anything that has weight (mass plus specific gravity) and occupies space. You can distinguish various kinds of matter by their properties: smell, color, weight, texture, melting point, boiling point, vaporizing point, and solubility in various liquids. The more properties of a substance you can identify, the more reliable your identification of the substance itself becomes.

Some kinds of matter require many tests to identify, others only a few. Suppose you have some white powder that may be either silver chloride ($AgCl$) or lead chloride ($PbCl_2$). They look very much alike, are both chlorides of a metal, and are the same color. However, lead chloride is entirely soluble in hot water, whereas silver chloride is only slightly soluble in hot water. In addition, silver chloride, when exposed to light, will go from white to a dark pinkish violet to black. A final, structural difference is that silver chloride consists of the linking up of silver and chlorine atoms at a 1-to-1 ratio, whereas lead chloride has a linking-up ratio of one lead atom to every two chlorine atoms.

A type of matter can also be grouped according to whether it is a solid, a liquid, or a gas. Most types of matter can be changed into any of these three states, given the necessary temperature and pressure. The liquid state is the normal intermediate step between solid and gaseous states. However, some matter will sublimate—that is, pass directly from a solid to a gaseous state or vice versa, without ever becoming a liquid.

Compounds

Compounds are substances that are uniform throughout and that comprise two or more elements. For example, rust (Fe_2O_3) is a compound of iron and oxygen; water (H_2O) is a compound of hydrogen and oxygen; and sulphuric acid (H_2SO_4) is a compound of hydrogen, sulphur, and oxygen. Each substance in each compound is present in definite proportions by weight as well as by quantity of atoms, thus distinguishing one compound from another. This is the law of definite proportions. If you take several samples of the same compound, in each sample—regardless of its size—the proportions by weight of each of the substances in the compound will prove to be exactly the same.

Water's weight is 88.9% oxygen and 11.1% hydrogen, whether you are talking about 1 drop, 1 gallon, or 100 gallons. These are the constant weight percentages of the compound we call water. If you vary the percent weights, even though using the same constituents (hydrogen and oxygen), you produce a different compound. Hydrogen peroxide (H_2O_2), for example, has the same constituent elements as water, but in a different structural arrangement and with altered weight percentages. The atomic weight of the compound has changed, and the structural formula now looks like $H{-}O{-}O{-}H$. The prefix "per-" in peroxide denotes an excess of the normal amount of the element to which it is affixed (in this case, oxygen) in the compound. Hydrogen peroxide in concentrated solutions is highly toxic.

Compounds are produced by various processes, chemical and mechanical, using various reagents and catalysts. Some widely used compounds are by-products of other processes or actions. Ferrous sulphate ($FeSO_4 \cdot 7H_2O$) is largely a by-product of the sulphuric acid pickling of steel (the acid dissolves some of the steel to produce ferrous sulphate).

Some compounds are very stable and some very unstable.

Mixtures

Mixtures differ from compounds in that they are not chemically combined with each other. They can be combinations or two or more substances or two or more compounds. Each constituent of a mixture retains its original individual properties, regardless of its proportion in the mixture, which can be variable. If you mix sand and walnuts together, you have a walsand or sandwal mix in which nothing has changed; and if you separate the two, the sand is still sand and the walnuts are still walnuts.

Some mixtures, when given a little nudge, become compounds. If you mix silver particles with powdered sulphur, you have a mixture; but, with a little heat and moisture (H_2O), you can cause a chemical bond to form between the sulphur and the silver, resulting in a compound, silver sulphide (Ag_2S). This compound no longer resembles powdered sulphur or silver: It is a grayish black powder. The suffix "-ide" in sulphide denotes a binary compound of an element (silver) with sulphur.

Some things, like gray cast iron, are part compound and part mixture. Some of the carbon in gray cast iron is chemically combined with the iron as iron carbide (Fe_3C), also called cementite, and some is simply mixed in the iron as free graphite, called graphitic carbon.

The proportion or ratio of cementite to free carbon in a given cast iron is dependent on several factors: the total carbon in the iron, the cooling rate of the material from liquid to solid, and the quantity of silicon present. The silicon and the freezing rate are the reagents that determine how much of the cast iron is chemically combined iron and carbon (a compound) and how much of it is simply a mixture of graphite and iron. The particular physical properties desired are achieved by controlling this action.

Nature forms many compounds from mixtures. The green patina that forms on cast bronze statues outdoors is a product of airborne sulphur and sulphurous compounds that change the copper on the surface of the bronze to copper sulphate or copper carbonate.

Atoms are simply defined as the smallest uniquely structured particles of which an element is composed, or as the smallest particle of any element that can enter into a chemical reaction. Atoms themselves are composed of still smaller particles:

electrons (negatively charged) and protons (positively charged). It is these charged particles, plus uncharged neutrons, that are responsible for the atomic weight of each element.

A molecule is the smallest particle of a compound that can exist and still retain the properties of the compound. When an element exists as a molecule, it usually consists of two or more atoms of that element (free hydrogen as H_2, and chlorine as Cl_2, for example). A molecule described as existing and still retaining the properties of the original compound must be existing independently.

Both physical changes and chemical changes produce some form of energy. Some physical changes are temporary. If you dissolve a salt in water, you get a physical change that you can reverse by evaporating the water and recrystallizing the salt. Although chemical changes are said to be more or less permanent, they, too, can usually be reversed. If you oxidize metallic lead in air to form lead oxide (litharge—PbO), you have formed a chemical compound of lead and oxygen that you can reverse under the blow pipe on the charcoal block, in a reducing flame.

The reaction called a "reduction" in this case is quite simple. The oxygen and carbon combine to form carbon monoxide (CO), which chemically combines with the oxygen of the litharge (PbO) to produce carbon dioxide (CO_2) and metallic lead. The reagents here are carbon and oxygen. The energy produced is the heat of the combustion oxidation of the carbon.

If you dissolve a small piece of copper in sulphuric acid, you produce heat energy. This heat energy is the product of the oxidation of the copper molecules by the oxidizing sulphuric acid, the chemical product being the compound copper sulphate ($CuSO_4$).

Conservation Rule

In every chemical reaction, the total weight (mass) of all the substances resulting from the change or reaction is exactly equal to the weight of all the substances entering into the reaction. If you were to neutralize sulphuric acid with sodium hydroxide, you would produce two new compounds, sodium sulphate and water. Expressed as a balanced chemical equation, this reaction is $5H_2SO_4 + 10NaOH \rightarrow 5Na_2SO_4 \cdot 10H_2O$.

The total atomic weight of the left side of the equation, $5H_2SO_4 + 10NaOH$, is exactly the same weight as the new compound ($5Na_2SO_4 \cdot 10H_2O$) produced by the chemical operation of neutralizing the sulphuric acid with the base, sodium hydroxide (lye). In this case, you produce a product called Glauber's salt (salt cake), used in the manufacture of soap, and water by the double decomposition of the original compounds.

When you dissolve silver in nitric acid, you produce silver nitrate solution and free hydrogen gas; if you add sodium chloride to this, you produce a precipitate of silver chloride (a solid white powder consisting, by weight, of 75.2% silver and 24.8% chlorine) and a soluble compound of sodium nitrate. What occurs is an ion exchange based on electrical potential differences between the ions of the compounds involved. Both sides of the reaction equation must be of equal weight. Written as balanced chemical equations, the two reactions are

$$2HNO_3 + Ag_2 \rightarrow 2AgNO_3 + H_2$$
$$AgNO_3 + NaCl \rightarrow AgCl + NaNO_3.$$

Molecular Weight

Molecular weight is defined simply as relative molecular mass—the sum of the atomic weights of all the atoms that constitute a molecule.

If you look at water as H_2O, you have two atoms of hydrogen to each atom of oxygen or two parts by weight of hydrogen to one part by weight of oxygen. The atomic weight of oxygen is 15.99 (or, rounded off, 16) and of hydrogen is 1. The molecular weight of water is therefore 17.98 (or, rounded off, 18)—the sum of the three atomic weights involved in a water molecule. For every 18 units (by weight) of water, whether the units are milligrams or tons, the ratio by weight of oxygen to hydrogen is 16 units to 2 units, or 88.9% to 11.1%. This property of elements is an invaluable aid in obtaining a solution of a desired molar weight (concentration).

You will be working with various concentrations of solutions and reagents and will often come in contact with formulas that call for particular molar concentrations of a solution. These formulas commonly include a term N (normal), 0.5 N or $N/2$ (half normal). 0.1 N or $N/10$ (one-tenth normal), 2 N (twice normal), and so forth. The meaning is simple: A normal solution consists of the weight in grams that is equivalent to the molecular weight of the substance to be put into solution.

Commonly, you will deal with gram equivalent weights of acids and of bases. In the case of an acid, the gram equivalent weight equals the molecular weight of the acid involved, divided by the number of replaceable hydrogen atoms present in that acid.

For example, if you wanted to make a N (normal) solution of sulphuric acid you would first have to determine its molecular weight, which is the sum of the atomic weights of its constituent elements. A molecule of sulphuric acid (H_2SO_4) is composed of two atoms of hydrogen, one atom of sulphur, and four atoms of oxygen. The atomic weights of these elements, as given in the standard periodic table of elements, are 1.0079 for hydrogen, 32.06 for sulphur, and 15.999 for oxygen. After doubling the weight of the hydrogen and quadrupling the weight of the oxygen, you can reach a sum for the molecular weight of H_2SO_4 93.065.

This number is divided by 2, as there are two replaceable hydrogen atoms, to derive the gram equivalent weight, 49.03. At this point, you know that if you add 49.03 g of sulphuric acid to 1 L of distilled water, you will have created a normal (*N*) 1-molar solution of sulphuric acid, which would be notated as 49 g/L (49 g per liter).

If you add 98 g/L instead, you will have created a 2 *N* solution; and if 24.5 g/L, a 0.5 *N* or *N*/2 solution is created.

The gram equivalent weight of a salt is derived by dividing the formula (or molecular) weight (the sum of the atomic weights of each constituent atom in the molecule) by either the total valence of the positive components or the total valence of the negative components. Salts are neutral compounds—that is, the positive and negative valences of their components have canceled out each other. It is, therefore, unimportant whether you choose to use the negative valence ions or the positive valence ions to ascertain the salt's gram equivalent weight; both sets of ions will always have equal absolute values. For example, sodium sulphate (Na_2SO_4) has two Na ions, with a valence of T + 1 each, and an SO_4 ion with a valence of − 2. Given this, you would take the molecular weight for sodium sulphate, which is 142.02, and divide it by 2, making the figure for the gram equivalent weight of Na_2SO_4, 71.01.

Aluminum sulphate [$Al_2(SO_4)_3$] is another salt. Its two Al ions have a valence of + 3 each, and its three SO_4 ions have a valence of − 2 each. Following the same pattern as above, you would take the molecular weight of a molecule of the salt (342) and divide it by 6, the absolute value of both the positive and the negative valences involved. The result is 57, which is the gram equivalent weight for aluminum sulphate. Fifty-seven grams of this compound per liter of distilled water will produce a 1-molar *N* solution of aluminum sulphate.

In the case of a base, each hydroxide (OH) is chemically equivalent to one hydrogen ion or atom. Therefore, for a base such as sodium hydroxide (NaOH) or calcium hydroxide [$Ca(OH)_2$], the gram equivalent weight is the molecular weight divided by the number of hydroxides—in the first case, 1, and in the second case, 2. Sodium hydroxide has one Na atom, with an atomic weight of 22.98, one O atom with a weight of 15.99, and one H atom with a weight of 1, making a total of 39.97. This molecular weight is divided by 1 (the number of hydroxides) to derive the gram equivalent weight. What it means is that if you dissolve 39.97 g of sodium hydroxide in 1 L of distilled water, you will have created a 1-molar normal (*N*) solution of sodium hydroxide.

The equivalent weight of calcium hydroxide is the sum of atomic weights of one Ca atom (40.8), two O atoms (15.9 each), and two H atoms (1 each) divided by 2 (the number of hydroxides in one molecule). Thus, you will find that the molecular weight of the compound is 73.8 and the gram equivalent weight is 36.9. This means that 36.9 g of calcium hydroxide dissolved in H_2O—with enough H_2O added to make 1 L of liquid—will produce 1-molar *N* calcium hydroxide solution.

Elements combine to form compounds. Through decomposition, compounds can revert to their separate elements. For example, mercuric oxide (HgO) when heated decomposes to metallic mercury (quicksilver or Hg_2) and free oxygen

(O_2). The chemical equation $2HgO + \text{heat} \rightleftarrows Hg_2 + O_2$ simply means that the reaction is reversible.

A compound with a simple chemical notation, such as $CuSO_4 \cdot 5H_2O$ (copper sulphate), can have many names: sulphate of copper, cupric sulphate, blue vitriol, blue stone, and blue copperas. All are correct. However, the rule is that either the metal or (if the compound contains no metal element) the element closest in characteristics to a metal is placed first. Carbon dioxide, rather than dioxide of carbon, is the common name for CO_2.

Following the letters $CuSO_4$, which designate the composition of copper sulphate, there is a center dot and then $5H_2O$. This $5H_2O$ is called a radical, meaning a group of atoms (in this case constituting five water molecules) that maintains its identity through chemical changes that affect the structure of the rest of the chemical elements involved. Usually, radicals are incapable of independent existence—an example is NH_4, an ammonium radical. The $5H_2O$ here, however, is a free radical, capable of independent existence. Some free radicals have a short-lived independent existence, whereas others last much longer and are called long-life free radicals.

In the case of copper sulphate, $CuSO_4 \cdot 5H_2O$, the radical $5H_2O$ came from the sulphuric acid (H_2SO_4) solution used in the initial reaction. These five water molecules were transferred in the oxidation reaction: $Cu + H_2SO_4 + 5H_2O \rightarrow CuSO_4 \cdot 5H_2O + H_2S$.

The suffix "-ate," when used in an inorganic compound, indicates a salt whose metal (or radical) is in the highest oxidation state. Here, the salt is a salt of copper produced by the oxidation of the copper by sulphuric acid. Similarly, copper dissolved in nitric acid produces copper nitrate: $Cu + HNO_3 \rightarrow Cu\ (NO_3)_2 \cdot H_2O + N_2O_2$. The subscript 2 following the (NO_3) indicates that there are two NO_3 ions present in the copper nitrate.

Copper dissolved in hydrochloric acid becomes copper chloride. Hydrochloric acid is an aqueous solution of hydrogen chloride, which is a colorless, fuming, highly toxic gas with a suffocating odor. The chemical equation is not difficult: $Cu_2 + 4HCl \rightarrow 2CuCl_2 + 2H_2$. Copper chloride ends in the suffix "-ide." When a compound consists of only two named elements (or radicals), it is given this suffix to indicate that it is binary (composed of two things only).

Oxidation

Oxidation takes place in any reaction in which there is a transfer of electrons. The reduction and refining processes that I cover in this volume depend largely on ion exchanges involving oxidation and reduction; these always occur together or simultaneously. Reactions of reduction and oxidation are also called redox reactions. The substance that gains electrons is called the oxidizing agent. The substance that loses electrons is called the reducing agent.

In the equation $Fe + Cu^{2+} \rightarrow Fe^{2+} + Cu$, two negatively charged electrons are transferred from the iron atom to the copper atom; thus, the iron becomes oxidized by the loss of two electrons while the copper receives two electrons and becomes reduced (neutralized). This is a redox (double) reaction.

Obviously, if you simply place a sheet of copper and a sheet of iron together, nothing like this happens. The ions must be situated so that they can get together. As an example, take a piece of copper and dissolve it in a solution of sulphuric acid (H_2SO_4), one volume of acid to two volumes of distilled water. Now you have a solution of the acidic salt, copper sulphate ($CuSO_4 \cdot 5H_2O$).

Now, among other things, ions of copper are circulating in the acidic oxidizing solution. If you take a bright, shiny, grease-free nail and immerse it in the solution, you will get an instantaneous redox reaction. What happens is the surface of the nail (iron) is oxidized and transfers electrons to the copper ions. The copper ions receive the iron electrons and are reduced to metallic copper, covering the nail with a copper plating.

If you then remove the nail and wash it off, you will have a copper-plated nail. This is the basis of immersion plating when no outside electrical source is involved, only the electrical potential difference between the metal that is to be deposited and the metal on which it is to be deposited. If you left the nail in the solution longer, its copper coating would eventually stop increasing in thickness. This occurs when the entire system (plated nail plus ionic solution) achieves its reaction end point (or chemical equilibrium). At this point, no exposed iron remains to be oxidized, and no additional copper is being reduced.

Reduction is, then, the opposite of oxidation—the other side of a redox reaction. It may occur in several ways: through the acceptance of one or more electrons by an atom or ion; through the removal of oxygen from a compound (deoxidizing); or through the addition of hydrogen to the compound.

A base is the opposite of an acid and reacts with an acid to form a salt and water only. Any substance that has a tendency to accept protons can be classed as "basic."

A base dissolved in water yields negatively charged hydroxyl (OH) ions. The presence of hydroxyl ions is the cause of the chemical properties of alkaline solutions. Basic compounds that are water soluble, such as sodium and potassium, produce the hydroxyl ion in considerable concentration. Water-soluble bases characteristically have a bitter taste and a slippery feel. Bases turn litmus paper blue because they are alkaline. There was a saying in the lab: "Alkaloo turns litmus blue." Examples of bases are sodium hydroxide or caustic soda (NaOH), potassium hydroxide (KOH), and ammonium hydroxide (NH_4OH).

A basic solution is strong or weak according to the fraction of molecules that break down into positive ions and into negative (hydroxyl) ions in solution. The strength or weakness is expressed as a pH, using pH paper or a pH instrument.

The pH of a solution is the measure of how acidic or basic the solution is. It is founded mathematically on the logarithms of the reciprocal of the hydrogen ion concentrations. The formula can be expressed as $pH = \log 10(1/[H^+])$.

Pure water is the (neutral) standard, using the exponent number without a positive or negative sign as the pH number. Pure water has a concentration (in grams per liter) of oppositely charged ions that is equal to 1/10,000,000 or, in scientific notation, 1×10^{-7}. Taking the exponent, – 7, and removing the negative sign, you can see that 7 is the pH of distilled water. The pH scale runs from 1 to 13. The range of acids is from 1 to 6.9; a pH of 1 indicates a very strongly acidic solution, whereas a pH of 6.9 denotes an extremely weak acid. The range of bases is from 7.1 to 13 pH; a substance of pH 7.1 is a very weak base, whereas one of pH 13 is an extremely strong base.

When you have acids or bases in a pure water solution, they ionize more or less completely, giving various concentrations of H^+ ions and OH^- ions. This is the concentration indicated by the pH number.

Control of the pH of a solution is extremely important in precipitations, electrorefining, electrowinning, and electroplating. To change the pH value of a solution, you add a base or acid to the solution. If you have an acid and want to weaken it, simply add a base; if you want to strengthen it, add a more concentrated acid. The reverse process works if you have a base.

The differences between pH numbers are misleading because the scale is logarithmic, not arithmetic. The difference between a pH of 3 and a pH of 2 is actually 90,000 units in the ratio of H^+ ions (in solution) to pure water. A small change up or down in the pH number is actually a large change in the number of positive or negative ions in a given solution.

The pH of a particular solution can be roughly gauged by what are called pH papers. These chemically treated papers, when dipped into a solution, change color. The color can then be matched against a color chart that comes with the paper. The matching color on the chart has an approximate pH value printed beside it. Litmus paper offers a very general indication of whether a solution is acidic or basic.

A pH of 7 is not always the correct end point of a titration. A large family of pH indicators exists that can be used for various types of reactions. When one is put into a solution and the solution is then adjusted to or reaches the indication point of that particular indicator, a color change occurs, indicating that the desired action is complete. Examples of such pH indicators are methyl orange, methyl red, and thymol blue. Electronic pH instruments are available, although these are not necessary for the processes covered in this volume.

Valence

When you dissolve an acid, a base, or a basic or acidic salt in water, it becomes broken up or dissociated into ions. These ions are simply electrically charged atoms or groups of atoms. The positively charged ions (+) are called cations; they have fewer electrons than is necessary for them to become neutral (that is, to cancel out their electrical charge or potential). The negatively charged ions (–), which are called anions, have excess electrons. The formation of ions by dissociation of acids, bases, or salts of acids or bases is called ionization.

Take, for example, hydrochloric acid (HCl), which consists of one positive atom of hydrogen (H^+) and one negative atom of chlorine (Cl^-). The + superscript on the H indicates that its valence is + 1. The – superscript on the Cl indicates that its valence is – 1. This exact opposition of valences is the link or bonding glue between the H and Cl atoms that leads them to form HCl. Unlike electrical charges attract one another and like charges repel.

Adding hydrochloric acid to water causes the dissociation (ionization) of the HCl's two component elements. The hydrogen takes the form of positive hydrogen ions (cations) in the solution, and the chlorine takes the form of negative ions (anions) in the solution. The chemical equation is

$$\begin{array}{ccc} \text{HCl} & \rightleftarrows & H^+ + Cl^- \text{ (in } H_2O\text{)} \\ \text{(binary compound)} & & \text{(ionized solution)} \end{array}$$

The double arrows ($\rightleftarrows$) indicate that this reaction (like all instances of electrolytic dissociation) is reversible.

From this example, you can see that the valence of an atom or group of atoms is simply the number of positive or negative charges possessed by its ion. The valence values for the elements are shown on the periodic chart.

Valence is a numerical relation; it does not convey any information about the intensity of the affinity between combining atoms (that is, how strong or weak the atomic glue that joins them is). It just indicates the number of univalent atoms of another element that an element's atom can hold in combination.

Many elements are able to exert different valences under different circumstances. Copper, for example, can have a valence of + 1 or + 2. However, the valence of the atoms that the Cu is bonding with influences which valence the Cu will exert. When exposed to chlorine, for example, which has a normal valence of – 1, copper can only form the compound copper chloride ($CuCl_2$). Here, the Cu has obviously bonded with a valence of + 2.

The combining actions of elements are simple to figure when you know the valences of the elements involved. For example, carbon can have a valence of +2, +3, or +4, whereas oxygen always has a valence of –2. Because of carbon's variable valence, carbon and oxygen can combine as CO (carbon monoxide) or CO_2 (carbon dioxide). As carbon monoxide, carbon has a valence of +2; as carbon dioxide, carbon has a valence of +4.

Again, the valence of an element is the number of hydrogen atoms one atom of the element can hold in combination or displace. If the element's valence is – 2, then one atom of the element can hold two + 1-valence hydrogen atoms in combination; if the element's valence is + 2, one atom of the element can displace two + 1-valence hydrogen atoms.

Metals and metallic salts usually have positive valences. Other common elements and radicals have negative valences.

The first two tables below present the names and valences of some common elements and groups that will be mentioned or discussed in the course of this book. The third table simply shows the common forms of some multivalent metallic elements and their typical valences.

Valences of Some Elements

Aluminum (Al)	Valence +3
Antimony (Sb)	Valence 0, –3, +3, or –5
Arsenic (As)	Valence 0, –3, +3, or +5
Barium (Ba)	Valence +2
Bismuth (Bi)	Valence +3 or +5
Boron (B)	Valence +3
Bromine (Br)	Valence –1
Cadmium (Cd)	Valence +2
Calcium (Ca)	Valence +2
Carbon (C)	Valence +2, +3, or +4
Chlorine (Cl)	Valence –1, +3, +5, or +7
Copper (Cu)	Valence +1 or +2
Fluorine (F)	Valence –1
Gold (Au)	Valence +1 or +3
Hydrogen (H)	Valence +1
Indium (In)	Valence +1, +2, or +3
Iodine (I)	Valence –1
Iridium (Ir)	Valence +3 or +4
Iron (Fe)	Valence +2, +3, +4, or +6
Lead (Pb)	Valence +2 or +4
Magnesium (Mg)	Valence +2
Manganese (Mn)	Valence +1, +2, +3, +4, +6, or +7
Mercury (Hg)	Valence +1 or +2
Nickel (Ni)	Valence 0, +1, +2, or +3
Nitrogen (N)	Valence –3 or +5
Osmium (Os)	Valence 0, +3, +4, +6, or +8
Oxygen (O)	Valence –2
Palladium (Pd)	Valence +2, +3, or +4
Phosphorus (P)	Valence +3 or +5
Platinum (Pt)	Valence +2, +3, or +4
Potassium (K)	Valence +1
Rhodium (Rh)	Valence +2, +3, +4, +5, or +6
Silicon (Si)	Valence +4
Silver (Ag)	Valence +1 or +2
Sodium (Na)	Valence +1
Sulphur (S)	Valence –2, +4, or +6
Tellurium (Te)	Valence +2, +4, or +6
Tin (Sn)	Valence +2 or +4
Zinc (Zn)	Valence +2

Valences of Some Ionic Groups

Acetate ($C_2H_3O_2$)	Valence −1
Bicarbonate (HCO_3)	Valence −1
Bisulphate (HSO_4)	Valence −1
Carbonate (CO_3)	Valence −2
Chlorate (ClO_3)	Valence −1
Hydroxide (OH)	Valence −1
Hypochlorite (ClO)	Valence −1
Nitrate (NO_3)	Valence −1
Nitrite (NO_2)	Valence −1
Perchlorate (ClO_4)	Valence −1
Permanganate (MnO_4)	Valence −1
Phosphate (PO_4)	Valence −3
Phosphite (PO_3)	Valence −3
Sulphate (SO_4)	Valence −2
Sulphite (SO_3)	Valence −2

Valences of Some Forms of Multivalent Metallic Elements

Antimony	(Sb)	as an antimonite	Valence +3
Antimony	(Sb)	as an antimonate	Valence +5
Arsenic	(As)	as an arsenite	Valence +3
Arsenic	(As)	as an arsenate	Valence +5
Bismuth	(Bi)	as a bismuth salt	Valence +3
Chromium	(Cr)	as a chromous salt	Valence +2
Chromium	(Cr)	as a chromic salt	Valence +3
Chromium	(Cr)	as a chromate	Valence +6
Cobalt	(Co)	as a cobaltous salt	Valence +2
Cobalt	(Co)	as a cobaltic salt	Valence +3
Copper	(Cu)	as a cuprous salt	Valence +1
Copper	(Cu)	as a cupric salt	Valence +2
Gold	(Au)	as an aurous salt	Valence +1
Gold	(Au)	as an auric salt	Valence +3
Indium	(In)	as an indium salt	Valence +3
Iron	(Fe)	as a ferrous salt	Valence +2
Iron	(Fe)	as a ferric salt	Valence +3
Lead	(Pb)	as a lead salt	Valence +2
Manganese	(Mg)	as a manganous salt	Valence +2
Mercury	(Hg)	as a mercurous salt	Valence +1
Mercury	(Hg)	as a mercuric salt	Valence +2
Nickel	(Ni)	as a nickelous salt	Valence +2
Nickel	(Ni)	as a nickelic salt	Valence +3
Palladium	(Pd)	as a palladous salt	Valence +2
Palladium	(Pd)	as a palladic salt	Valence +4

Platinum	(Pt)	as a platinous salt	Valence +2
Platinum	(Pt)	as a platinic salt	Valence +4
Rhodium	(Rh)	as a rhodium salt	Valence +3
Silver	(Ag)	as a silver salt	Valence +1
Tin	(Sn)	as a stannous salt	Valence +2
Tin	(Sn)	as a stannic salt	Valence +4

In all your metallurgical work, you will find it advantageous to have a good general chemistry text.

Chemistry is not really that complex, difficult to understand, or learn. The more you understand and have a good grasp of, the less problems you will encounter, and those problems you encounter will be easier to solve as your knowledge of chemistry increases. The study of chemistry and metallurgy is a continuous endeavor. The easiest way to study and understand the subject is to break it down into systems. When you understand how each system works, the relationship between them becomes clear and all of it then makes sense. This is, however, not the way chemistry is taught today. It is taught in a way that is most confusing. One can only imagine that this is an attempt by the instructor to impress the student on the cleverness of the instructor. If you compare a chemistry text written 40 years ago against one written lately, this all becomes quite apparent.

The Systems

1—Chemical Change. 2—Electrical Chemistry. 3—Bonds. 4—Acids and bases. 5—Water.

Change

If we compare the initial state of a system to the final state of the system, we are studying change. Change in a system can go forward in one step or several, or reverse. If we have a formula like $A + B \rightleftarrows C + D$, the arrows indicate that when A is combined with B, it changes to C+D. However, in this case, the change from A + B to C + D can be reversed back to A + B.

This is not always the case. If you ignite gun powder, you produce a very fast reaction, rapid oxidation of the carbon and sulphur, resulting in an explosion. There is no way to reverse the change (reaction). See Figure 2.1.

In many cases, it requires several different reactions to reverse the change back to the original starting point. For an example, see Figure 2.2 in which we have changed metallic silver Ag° to a solution of silver nitrate. If we evaporate the solution we have luna salts (silver nitrate). Now, if we wish to reverse all this in order to make the silver in our solution back into Ag° metallic silver, we have to put the system through the changes shown in Figure 2.3. We are back home with our silver.

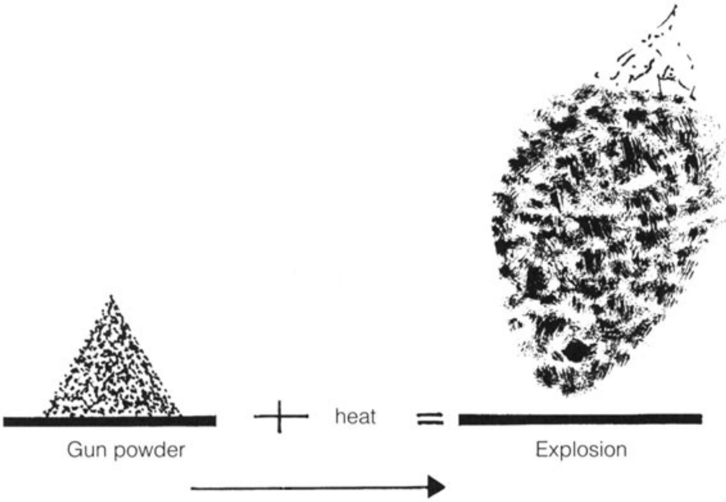


Figure 2.1. Reaction of heat applied to gunpowder

In refining precious metals, you are going to be faced with lots of these change reactions, depending on what you have and in what state it might be. See Figure 2.4. Here, we have a reversible reaction or change. If we dry the iron oxide, we simply remove the moisture (HOH). The iron bonded to oxygen (rust) remains the same. To get back to Fe° metallic iron from rust, it becomes obvious that we have to somehow remove the oxygen from the iron: $FeO + ? \rightarrow ??$. If you are knowledgeable in chemical changes, then several solutions will come to mind as to how to solve the problem. For $FeO + Al$ + ignition → Fe° (metallic) + AlO, we have simply transferred the oxygen from the rust (FeO) to the aluminum, making aluminum oxide, a Thermit reaction.

This change is called a reduction reaction or $FeO + C$ + heat → $CO + CO^2$ + Fe° (metallic). We could also accomplish this via wet chemical method. It amounts to what change you wish to make and how to go about it. Earlier, we see that a metallic oxide can be reduced to metal (that is, CuO to copper metal, etc.). You must, however, look carefully at the rate (speed) of the reaction. For example, you can, without danger, reduce the oxides of iron, copper, and chrome

Figure 2.2. Nitric acid + metallic silver = silver nitrate; reaction moves to the right

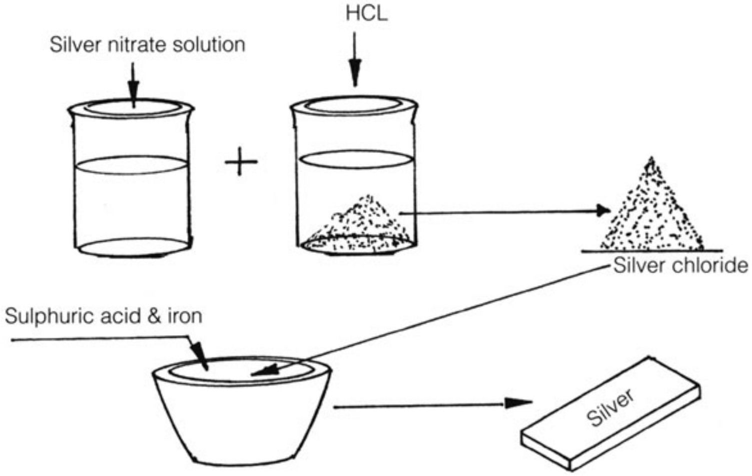


Figure 2.3. Reversing action in Figure 2.2 moves left back where we started

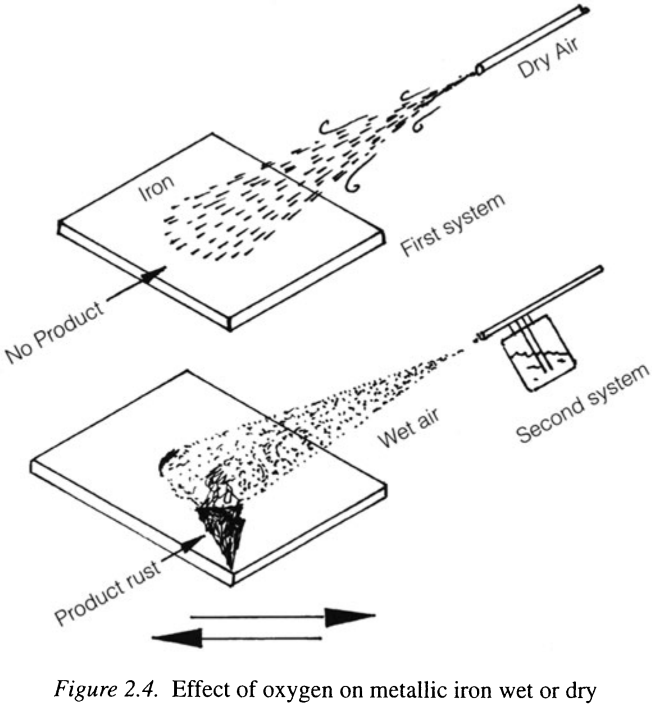


Figure 2.4. Effect of oxygen on metallic iron wet or dry

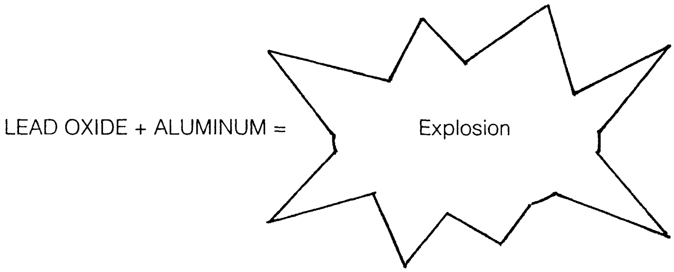


Figure 2.5. Explosion due to rapid reduction of lead oxide by aluminum powder and heat

via the Thermit route, using aluminum powder as the reducer (oxygen scavenger). Do not try to reduce PbO (litharge) to Pb° via this route. The oxygen is so loosely bonded to the Pb that the reaction is instantaneous, resulting in one "helluva" explosion (extremely dangerous). See Figure 2.5.

Electrical Chemistry

Electrical energy can be used in many ways; the ones that are more common to us all would be to operate a TV, radio, or CD, to start your car, and to furnish ignition for water heaters and motors (see Figure 2.6. It is also used in hundreds of ways to bring about chemical change. Millions of tons of chlorine and sodium hydroxide are produced every year by the electrolysis of sodium chloride solutions; see Figure 2.7.

With electrolysis, unlike heating water, starting your car, and the like, the metallic connections between the terminals of the source of electric energy are not continuous. The chemical reaction (change) takes place at the electrodes. See Chapter 6. Electricity can be produced chemically; see Figure 2.8.

The storage battery (the lead acid battery in your car) produces electricity by a chemical action which can be reversed by applying a charge to the battery from an external source—the car's generator. In the precious metal industry, a

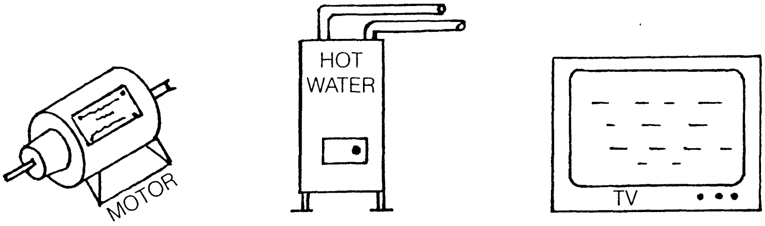


Figure 2.6. Uses of electrical energy

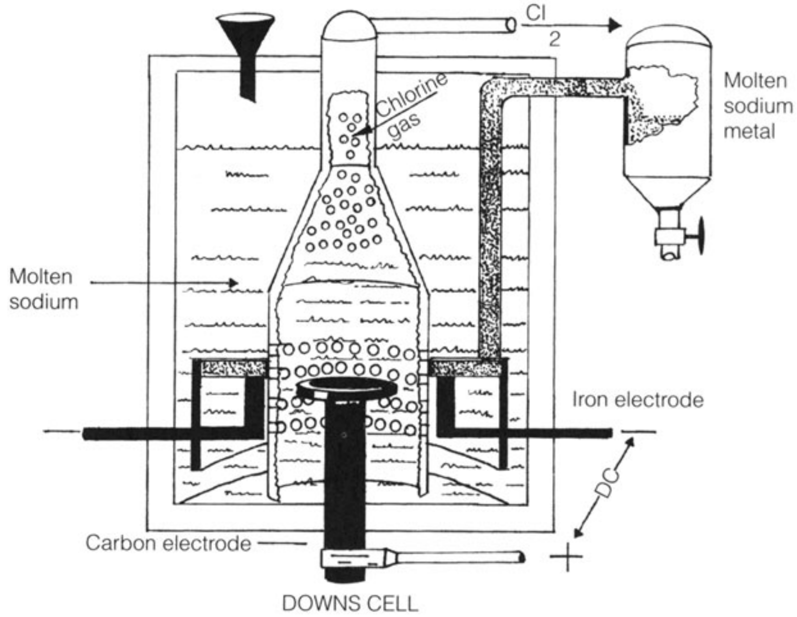


Figure 2.7. Cell used to produce chlorine (Cl_2)

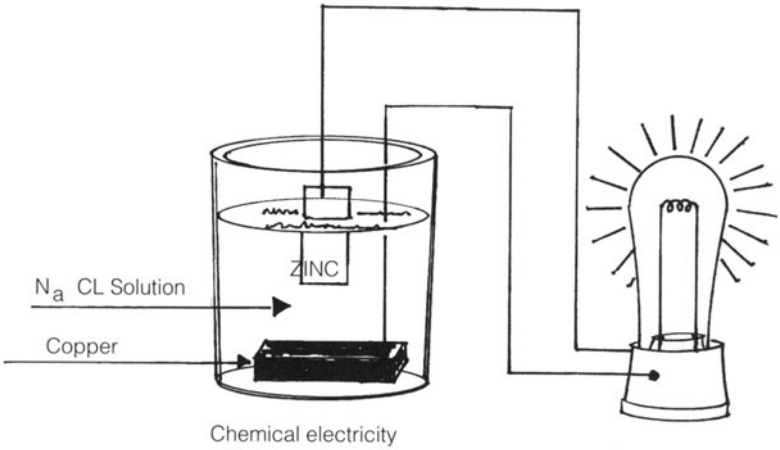


Figure 2.8. Chemically produced electrical energy

considerable amount of refining is done via electrical chemistry, usually referred to as electrowinning.

Bonds

This is the study of how various elements can form bonds with each other to form molecules. An atom of chlorine and an atom of sodium can form a bond to produce a molecule of NaCl (sodium chloride, table salt); 2 hydrogen atoms + 1 oxygen atoms = 1 molecule of water HOH or H_2O. Actually, you wind up with 2 molecules of H_2O—hydrogen $2H_2$, four atoms of hydrogen, and O_2. Two atoms of oxygen bond together to form two molecules of water, or 2HOH. Actually, we refer to water as H_2O not as 2 H_2O, which is the result:

$$2\ H_2 + 2\ O_2 = 4\ H \text{ and } 2\ O = 2\ HOH.$$

The study of the bonding of atoms is an extensive field and one could spend several lifetimes of effort in this direction. Examples are the following:

Chemical bond: sharing or transferring of electrons between two atoms

Ionic bond: transferring one or more electrons from the outer shell, normally between a metal and a nonmetal

Covalent bond: sharing of electrons; see Figure 2.9.

This book will not cover atomic theory. A very basic, easy-to-understand book which will give you an insight into atoms and molecules that you should have is *Marvels of the Molecule* by Lionel Salem.

Acids and Bases

Acid is defined as a chemical compound containing the element hydrogen and having the ability to supply positively charged hydrogen ions to a chemical

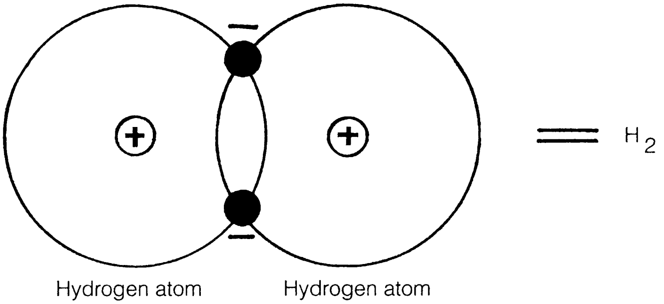


Figure 2.9. A hydrogen molecule (H_2)

reaction. There are many acids. For the most part, you will be dealing with three: nitric (HNO_3), sulphuric (H_2SO_4), and hydrochloric (HCl).

Bases are also called alkalies. This class of chemical compounds has the property of forming the ion OH^- in a solution. Bases are generally the opposite of acids; they neutralize acids, reacting with them to form salts. The term alkali salt originally came from the practice of making lye (sodium hydroxide) by leaching ashes of certain plant life which contained carbonates of sodium and potassium, such as sodium hydrooxide (Na–OH and potassium hydroxide (KOH) (hydroxide–OH).

The hydroxide salts are the products of leaching the ashes; then after evaporating the water, the salt was called caustic soda and was used, among other things, in the making of soap—Grandma's lye soap. It is still the basis of soap-making today. Today, the major source of hydroxides comes from alkali metals (i.e., sodium, lithium, potassium, rubidium, cesium, francium, the radical ammonium, and NH_4 Cl.

Ammonium hydroxide is produced by absorbing ammonia (a gas) in cold water. This gives ammonium hydroxide, a very caustic solution. All hydroxides have a pH of from 8 upward. A pH of 6 or below is acidic. All alkalies are water soluble. If you dissolve a piece of iron in hydrochloric acid and then add a caustic solution (or salts) to the iron HCl (acid solution), the pH will increase. You will reach a point where the iron will precipitate out as an orange red solid. You now have iron hydroxide. If you now add enough hydrochloric acid, you can reverse everything back to where you started: iron chloride $\rightleftarrows$ FeO = iron oxide, FeOH = iron hydroxide, FeOOH = iron oxyhydroxide. Here, you have an extra oxygen atom.

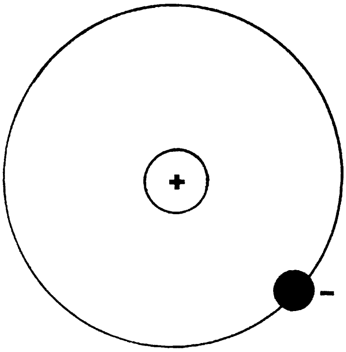
Now back to acids. Let us look at what is meant by the ability of an acid compound to supply positively charged hydrogen ions to a chemical reaction.

In a normal hydrogen atom, the nucleus contains one proton and one neutron with one electron in orbit around the nucleus. See Figure 2.10.

Now, if the hydrogen atom loses its lone electron, then you have a loose proton (H^+) and as this is not its normal state or condition for a hydrogen atom, it is very unstable chemically and most active. It is in this state (minus its electron), it thrashes around in search of a free electron for its electron shell. When it has accomplished this, we have what is called nascent hydrogen, which is in an abnormal active state. When it is in the H^+ state, consisting of a proton looking for an electron, this proton H^+ is what causes the stimulation to our tongue which we call sour or biting (that is, vinegar, citric acid, etc.).

Once H^+ has located an electron for its K shell, its nascent hydrogen wobbles about out of control; when it finds another nascent hydrogen, it forms a covalent bond, each sharing its lone electron with its neighbor for balance and stability. We now have hydrogen's normal state of two nascent hydrogen atoms bonded together, H^2.

A similar condition exists for oxygen (O, O_2, and O_3), O being nascent oxygen



Nascent hydrogen atom

Figure 2.10. A single hydrogen atom (nascent)

with six electrons in the L shell and very active and unbalanced. Here, again, two nascent oxygen atoms will join together via a covalent bond to give you O_2. Most atoms desire to fill their L shells with eight electrons, and as oxygen has only six, it needs two for balance; therefore, two oxygen atoms get together and bond, which gives us O_2. O_3 is O_2 with an extra nascent oxygen hanging on very loosely. This is called ozone. Thus, two nascent hydrogen atoms bond to form H_2, a molecule of hydrogen and two nascent oxygen atoms bond together to form O_2, a molecule of oxygen. Two H_2's + one O_2 forms two molecules of water, 2 HOH.

The new theory of acids and bases (alkalines) states that acid is any substance that gives protons; a proton donor (H^+ ions) and alkalines are proton receptors. So now what we have is that any solution is either more acid or more alkaline. If a solution is more acidic than alkaline, it is called acidic or acid. If it is more alkaline than acidic, it is referred to as basic or alkaline. It depends on which characteristic dominates, acid or basic. Now that makes sense, as all acids have some alkaline factors and all alkalines have some acid factors, therefore there is no absolute acid or absolute alkaline.

This makes pH 7 (neutrality) an ideal condition where acid (H^+) and alkalinity (OH^-) are equal amounts.

Water (HOH)

Water is the normal oxide of hydrogen. Pure water (deionized water) is a colorless, odorless liquid, whose melting point is 0°C and boiling point is 100°C; maximum density at 4°C of 1.00 g/cc water consists of associated H_2O due to hydrogen bonds between molecules. See Figure 2.11.

Water's allotropic forms are ice and steam. Allotrophy is the phenomenon of

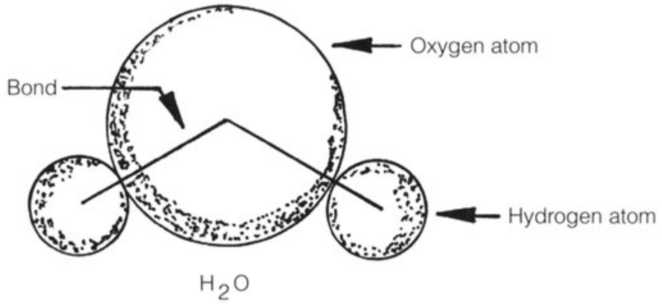


Figure 2.11. A water molecule (HoH)

an element having two or more forms without a change of state between the forms. Water is a polar liquid with high dielectric constant (81 at 17°C). This accounts for its solvent power. One gallon of water at 15° weighs 8.337 lbs. Derivation 1—oxidation of hydrogen, 2—end product of combustion, 4 end product of condensation reaction. Water is the most important reagent a chemist possesses. It has many, many uses (that is, hydrolysis, power source, source of hydrogen by electrolysis, thermochemical decomposition, etc.). By far its greatest use in the chemical industry is as a solvent.

The water molecule (see Figure 2.11) looks like a tennis ball (oxygen atom) to which two marbles have attached themselves (hydrogen atoms). The connection between the hydrogen atoms and the oxygen atom is called a bond. The bonds in a water molecule are so strong that a drop would have to be heated to over 2000°C (3632°F) in a very special furnace in order to break the molecules into their component atoms, H and O.

A million, million, million, million (10^{12}) water molecules are needed to make up a drop of water.

Rules of Solubility in Water

The rules of solubility are as follows:

A. Common sodium potassium and ammonium are soluble in water
B. Common nitrates, acetates, and chlorates are soluble.
C. Common chlorides are soluble except silver, mercurous, and lead (lead chloride is soluble in hot water). This fact is used to remove lead chlorides from silver chlorides.
D. Common sulfates are soluble in water, except calcium, barium, strontium, and lead.
E. Common carbonates, phosphates, and silicates are insoluble, except sodium, potassium, and ammonium.
F. Common sulfides are insoluble, except calcium, barium, strontium, magnesium, potassium, and ammonium.

3

Testing, Identification, and Familiarization

It is extremely important that you become well versed in the testing and identification of primary and secondary metals, minerals, and elements in all their possible forms. These forms include solid metals, oxides, sulphides, metallic salts, chlorides, nitrates, and (in aqueous solutions) metallic ions. Some tests and identifying procedures are in reality miniature extractive and refining operations, which relate to the full-scale operations covered in this volume.

Some tests are qualitative and some are quantitative. Whenever possible, you should take known samples and put them through the tests for unknown substances. In this way, when you are testing something that really is unknown, you will be able to recognize reactions, smells, and so forth, and relate them to others you observed during your tests of known samples. In all extractive and refining operations, you will perform numerous tests.

Suppose that you are extracting or refining some scrap gold that you had thought was a simple alloy of copper and gold, and you come up with a white precipitate of silver or lead chloride. At once, you would recognize what had happened and why. Then, you could adjust your process and test further. It is definitely worthwhile to purchase or acquire a small quantity of various pure, known materials—platinum, gold, silver, and copper—and practice with them.

Take a very small piece of pure silver, put it into a test tube, and add a solution composed of equal parts (by volume) nitric acid and distilled water. Never add water to an acid; if you do, the acid will spit and react violently. Always add the acid to the water, *slowly.* The chemical dissociation of the ions produces heat (one product of an exothermic reaction). If the acid is added to the water in a large quantity and too fast, heat may be generated so fast that the containing vessel will burst. When large additions of an acid are required, you must only add a small amount at a time and let the reaction cool down in between. Always make sure you are not in the "line of fire." In test tube work especially, when

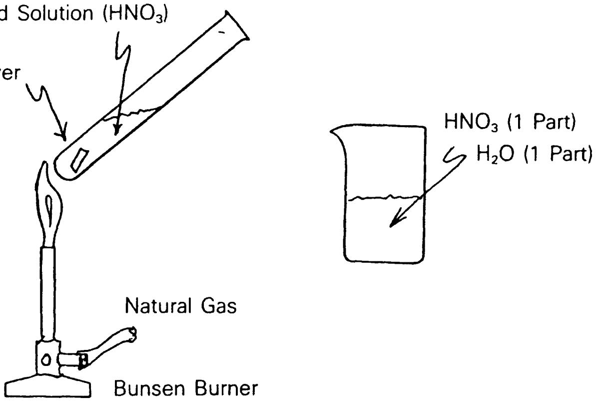


Figure 3.1. Dissolving silver in nitric acid solution

adding materials or when heating them, you can sometimes have the contents erupt out of the tube like a steam cannon.

Returning to the example, next heat the solution of nitric acid (and the silver sample in it) gently over a Bunsen burner or alcohol burner; the silver will soon go into solution. You now have a solution containing free silver ions. This is dissociation in the form of a salt dissolved in water. See Figure 3.1.

You have performed half of a redox—the oxidizing half—and you are left with a clear acid solution of silver ions. Now, drop a pinch of table salt (NaCl) or a little full-strength hydrochloric acid, drop by drop, into the solution. At once, a cloudy, curdy white precipitate is formed: silver chloride (AgCl). See Figure 3.2.

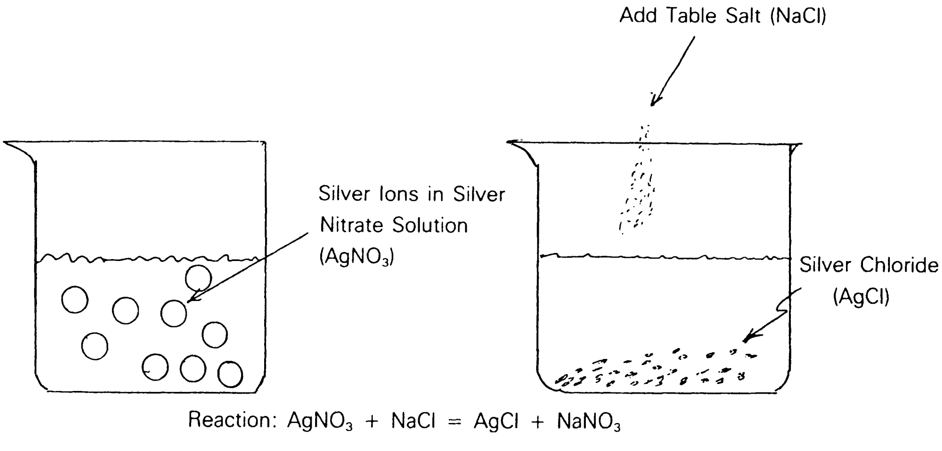


Figure 3.2. Precipitating silver chloride from silver nitrate solution

You now have a compound the molecules of which consist of one silver atom, with a + 1 valence, hooked to one chlorine atom, with a − 1 valence. The silver in this compound in no way resembles the metallic silver originally put into solution. However, the total weight of the silver you started with is still there. If, instead of adding chlorine (from table salt or hydrochloric acid) to the solution, you had simply hung a copper wire in the silver nitrate solution, the wire would have begun to dissolve slowly (go into solution), and the silver would have solidified on the partially dissolved wire in the form of pure metallic crystals. This process is called cementation. What you have undertaken instead are two separate steps in the process known as wet refining silver.

Now suppose that, in place of pure silver, you had a piece of sterling silver, which is supposed to be an alloy of 7.5% copper and 92.5% silver. How would you make certain of its purity? You would start by getting an exact weight for your sample; then you would dissolve the sample in a solution of equal parts nitric acid and water. This operation produces a green solution. The green is caused by copper ions that have been freed along with the silver ions in the solution. When you add chlorine to the solution, as you did in the pure silver example, down comes the same white precipitate of silver chloride; the copper ions stay in solution. If you then wash the silver chloride onto a filter paper and rinse any residual copper solution off of it with distilled water, until every bit of material on the filter is snow-white, you are left with the following state of affairs: The copper remains in solution and the silver now exists as a water-insoluble compound on the filter paper. See Figure 3.3.

If you were to hang an iron wire in the green solution, the copper ions would form copper crystals on the wire as the iron went into solution. This reaction or iron exchange is a somewhat different issue, however. What you have at the moment is a separation of the elements in a copper and silver alloy. Now, you can reduce the silver chloride to metallic silver and chlorine gas under the blow pipe, or you can convert the silver chloride to metallic silver plus an aqueous solution of another metal and chlorine by an ion exchange.

In the first example, with a known pure silver sample, you performed an acquaintance experiment. In the second example, with what was assumed to be a piece of sterling silver, you performed an extraction operation, separating the silver and copper. You still have not identified the specific composition of the second piece of metal, however.

Because you know the exact weight of the original sample of sterling silver, you can weigh the separated and reduced silver and subtract it from the original sample weight. This is one way of performing an assay. Once you have taken the copper out of solution, you can weigh it too. It the weight of the copper equals the difference between the original sample's weight and the weight of the pure silver, the original metal must have been entirely an alloy of silver and copper; and you need only compare the percentage weights you found for the two end products of your tests with those prescribed for silver and copper in

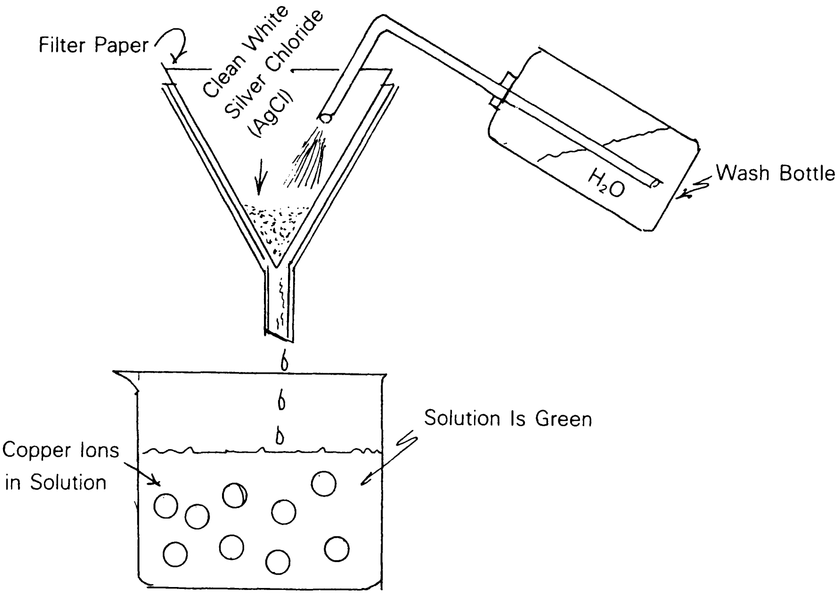


Figure 3.3. Washing silver chloride free of copper solution

sterling silver to discover whether your sample conforms to standards. Suppose, though, that the combined weights of the copper and silver do not equal 100% of the original sample's weight, but only 87.5% of it. Suppose also that the copper did account for its expected 7.5% of the original weight, but that the silver fell 12.5% short. What accounts for this? It could be that mercuric chloride ($HgCl_2$) or lead chloride ($PbCl_2$), both of which look like silver chloride, precipitated alongside the silver chloride. If you took the entirety of your first (white) precipitate and put it into a solution of ammonium hydroxide (NH_4OH), the portion of the white precipitate that was silver chloride would dissolve in the ammonium hydroxide, leaving behind the unknown white precipitate, which could then be identified by one of several other methods. The silver chloride in solution with ammonium hydroxide could then be recovered by neutralizing the ammonium hydroxide (a basic solution). This is easily done by using an amount of nitric acid slightly in excess of the ammonium hydroxide. Immediately, the silver chloride—this time, pure AgCl—would precipitate out again in its familiar curdy white form.

What you have done here, besides practicing separation and identification, is performed, on a miniature scale, a step in refining silver called repurifying. You can take scrap silver and refine it by changing it from silver nitrate to silver chloride to silver; you can repeat all three steps and upgrade the purity of the silver, or you can repurify the silver chloride by putting it into solution in ammonium hydroxide and then filtering this solution to catch any material not soluble in the ammonium hydroxide.

There are various grades of substance purity, including chemically pure (CP) (the highest grade), reagent grade (an intermediate grade), and commercial grade (a relatively low grade). Your choice depends on your intended use. The price depends on whether and how often the chemical, metal, or metallic salt has been purified. Distilled mercury, for example, will cost x dollars per pound; triple-distilled mercury will cost three or four times x.

The Blow Pipe

The blow pipe is a mouth-operated tube or device used to supply oxygen in support of combustion in such a manner that the conditions of the supplied combustion can be controlled by the operator. The blow pipe in one shape or another has been in use since about 4000 B.C. Evidence of this has been uncovered and pieced together from archeological diggings.

The ancient founder or metal worker reduced native ores from their natural forms (metal oxides) to a metallic state; in this state, they could be fashioned by hammering or molding into useful or decorative items.

What the early metal worker did was fill a bowl-shaped depression in the ground with charcoal (his fuel), ignite the fuel, and—when it was burning briskly—place his native ore or metallic oxides on the fuel. The combustion was increased in intensity by supplying additional oxygen to the fuel through a mouth-blown reed blow pipe. See Figure 3.4.

When metallic oxides are heated to a sufficient temperature in a zone where there is a deficiency of oxygen, the oxygen in the ore itself separates to help complete combustion, and this reduces the ore to an oxygen-free metallic state. The resulting metal drips down through the fuel to form a metallic slug or button, which, when cooled and solidified, is recovered and worked as desired.

Ancient metal workers learned that an ore could only be reduced to a metallic state if it were melted in a zone where there was a deficiency of oxygen and a sufficiency of carbon. The reason for this is that the oxygen in the metal oxide

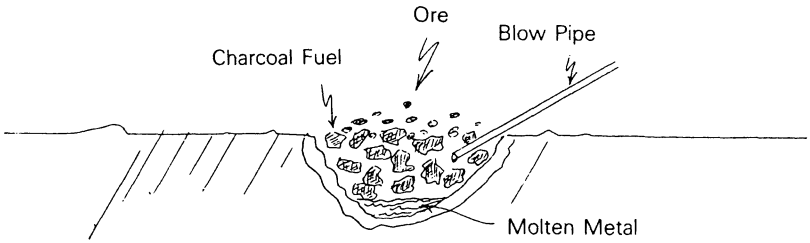


Figure 3.4. Ancient reed blow pipe in operation

is released only when there are free carbon ions present for it to join to form carbon dioxide, a product of combustion.

Should an ore that is a metallic oxide be raised to a high temperature in a zone containing excessive oxygen, it will not melt. If a metal in its pure state is melted or heated to a high temperature in a zone of combustion that contains excessive oxygen, it quickly oxidizes into a metallic oxide.

Extractive Metallurgy

The process of extracting metal from its ores is called extractive metallurgy. The extractive metallurgy of each metal presents peculiarities of its own.

Many ores are oxides of metals; others are carbonates, hydroxides, or sulphides of metals. Ores that are carbonates and hydroxides are generally reduced to metallic oxides by simple heating. This process is called roasting. They then can be readily reduced to metallic form by heating to a high temperature in the presence of carbon. Sulphide ores, however, must be heated or roasted in the presence of a current of air in order to be reduced to oxides.

Not all metallic oxides can be freed of their oxygen and reduced to their metallic state by heat and the presence of carbon. Chromium oxide (Cr_2O_3) is one such oxide. It, however, can be reduced with heat and the presence of aluminum. The chemical equation looks like: $Cr_2O_3 + 2Al \rightarrow 2Cr + Al_2O_3$.

Many metallic ores are found in many chemical forms. A good example is copper. Very little native copper in its metallic state is found. Common copper ores are copper oxide, copper carbonate, copper sulphide, and copper hydroxide.

Combustion

To understand the blow pipe completely and to use it efficiently as a simple means of identifying metallic and nonmetallic minerals, you must understand combustion.

The three conditions of combustion are reducing, neutral, and oxidizing. Reducing combustion occurs when the combustion lacks sufficient oxygen. Neutral combustion occurs when the combustion has the exact amount of oxygen necessary to combust all the fuel. Oxidizing combustion occurs when the combustion is supplied with an excess of oxygen.

Complete, neutral combustion is just about impossible, as it requires 100% efficiency. In any case, the concern of this book is with reducing or oxidizing flame reactions on minerals.

If you heat a sample of a metallic oxide under a blow pipe with a flame that is reducing (contains insufficient oxygen), the oxygen in the metallic oxide will be released to aid combustion, reducing the metallic oxide to a pure metallic state. If the sample is not a metallic oxide but a metallic carbonate, sulphide, or hydroxide, you must, of course, reduce it to an oxide first. This is accomplished by heating the sample in an oxidizing atmosphere (containing an excess of oxygen), which reduces it to a metallic oxide. Then, you can reduce the oxide as before, leaving the metal.

Fluxes

Besides controlling the products of combustion used in heating a mineral so that it oxidizes or reduces, you can employ chemical fluxes—compounds that aid in oxidizing or reducing.

A simple example of a chemical flux is saltpeter (potassium nitrate—KNO_3), which, when heated, gives off copious amounts of oxygen. Saltpeter is the chemical that supplies the oxygen for combustion in gunpowder. If you melt a piece of 14-carat yellow gold, which is 14/24 (58.33%) pure gold and 10/24 (41.67%) copper, in a small crucible and add some borax ($Na_2B_4O_7$) and saltpeter (KNO_3) to the molten gold, the oxygen in the saltpeter is released and combines with the copper in the melted gold alloy. This reduces the copper to copper oxide (Cu_2O), which enters the molten slag (borax), leaving the denser, pure gold behind to solidify into a metallic button.

The word "flux" comes from a Latin root meaning "to flow." Chemical fluxes are classified into four groups:

Oxidizing fluxes: These introduce oxygen and are used in removing oxidizable metals or impurities. Potassium nitrate (KNO_3) and sodium nitrate ($NaNO_3$) are the best of this group.

Reducing fluxes: These fluxes have an affinity for oxygen and will remove it from ores by reacting chemically with oxides that are already present. Examples of this type of flux are charcoal, sugar, dry sodium carbonate (Na_2CO_3), argol, dry potassium carbonate (K_2CO_3), potassium cyanide (KCN), phosphorus (P), and lithium (Li).

Neither reducing nor oxidizing fluxes: These fluxes act as covers to neutralize the oxidizing or reducing effects of the products of combustion during melting. They also dissolve and flux off any oxides that may be present. The commonest of these are borax ($Na_2B_4O_7$), boric acid (H_3BO_3), fluorspar (CaF_2), and powdered glass.

Tougheners: These are used in purifying gold that is almost pure already. Examples are ammonium chloride (NH_4Cl), mercuric chloride ($HgCl_2$), and copper chloride ($CuCl_2$).

Fluxes can be used to advantage, but if their proper reaction or use is misunderstood, they can cause problems. You must first ascertain exactly what reaction or conditions you wish to bring about, and then select the flux that will give you the desired results. You should practice with samples of known metallic and nonmetallic minerals.

Using the Blow Pipe

Modern blow pipes come in several sizes and shapes. Most, however, are simple, tapered, brass tubes, large at one end (into which you blow), and terminating in a bend that has a small hole at its point of discharge. See Figure 3.5.

Blow pipes are usually from 7 to 10 in. in length. Some have a small bulge or air reservoir, which is considered by some people (not by me) to make them superior to the common blow pipe; see Figure 3.6. Some blow pipes come in three pieces and can be taken apart to make a small package; see Figure 3.7. Another type uses natural gas as a fuel; at one time, this was a popular type for use in making jewelry. See Figure 3.8.

The blow pipe can be used with a candle or spirit lamp. In the field, a good candle is preferred because it is easy to carry and does not raise the problem of carrying alcohol, which you must have to use a spirit lamp. See Figure 3.9. If you do decide to use a candle, you should be aware that it must be made of a good, free-burning wax or tallow, and the wick must have the correct length and breadth in relation to the candle's diameter; see Figure 3.10. Whether you use a spirit lamp or a candle, the action of the blow pipe is the same.

Blowing the blow pipe seems a bit tricky, but with a little practice it can be mastered, and you will be able to produce a desired flame for a considerable length of time with little or no fatigue.

The idea of "blowing" the blow pipe is actually somewhat misleading: the force for the passage of air through the blow pipe comes not from the lungs but from the cheeks, which are distended (puffed out) and act like a bellows. The trick is to supply a continuous and even flow of air through the blow pipe. Two steps are essential: breathe through your nose and keep cheeks distended. Air flows through the blow pipe due to the tendency of the distended cheeks to collapse.

Practice breathing through your nose, with your mouth closed and your cheeks distended (do this before a mirror). When you can do this for a considerable period of time, slip a blow pipe between your lips, and you will find that a steady flow of air from the blow pipe can be maintained. Remember not to blow with your lungs nor to collapse your cheeks. Your cheeks must remain distended and relaxed.

The blow pipe can only be mastered when you can completely relax. If you have false teeth, you really have to relax (as anyone with "china clippers" knows) because air under the plate is bad news. When you have mastered a continuous, steady air delivery from the blow pipe, you are ready to do it in actual practice.

The object of this whole process is to produce a long, pointed, controlled flame from the candle that can be directed where you desire it. Light the candle and study the flame. You will find that it consists of three distinct zones: an oxidizing or yellow flame, a reducing or blue flame, and unburned gas. See Figure 3.11.

Now, with the blow pipe, blow into the flame, causing it to extend in a long

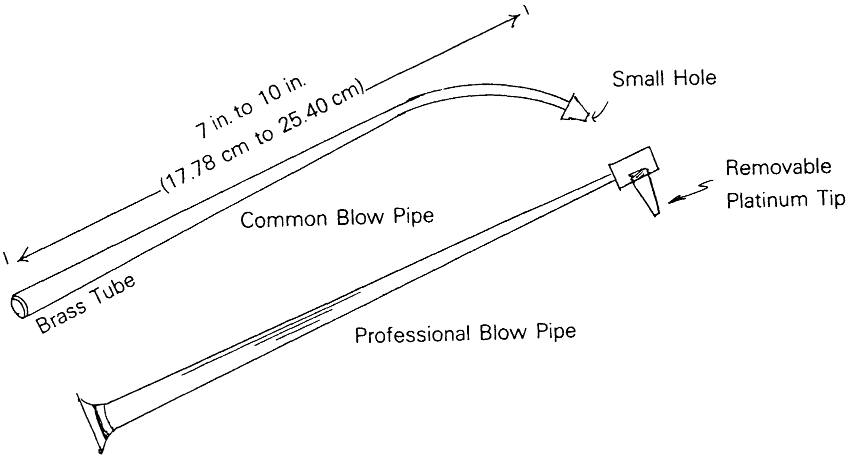


Figure 3.5. Blow pipes

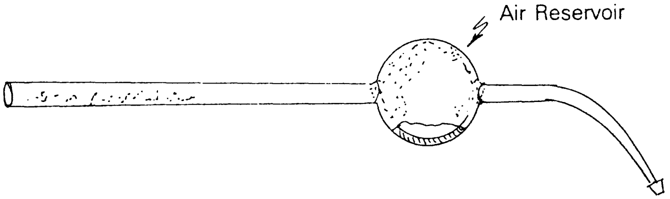


Figure 3.6. Air reservoir blow pipe

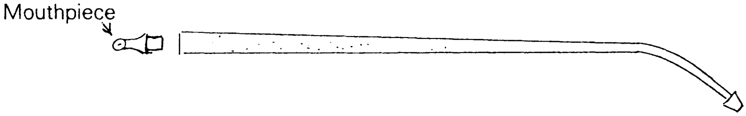


Figure 3.7. Removable mouthpiece blow pipe

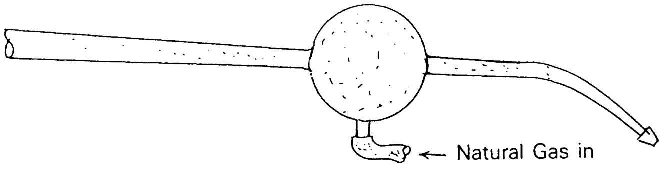


Figure 3.8. Gas-assist blow pipe

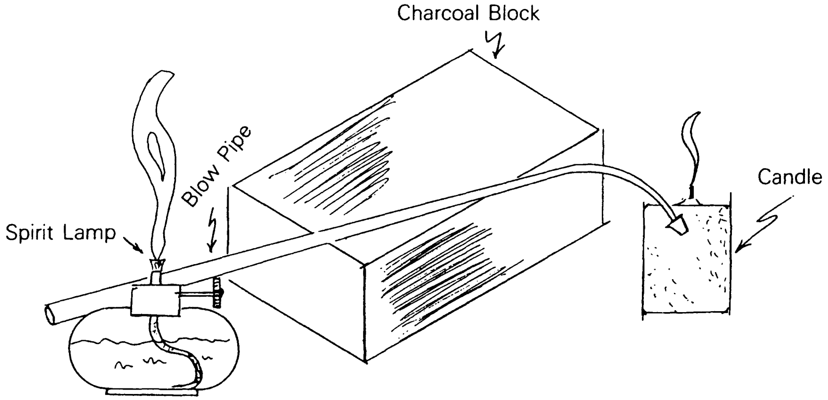


Figure 3.9. Basic tools for work with the blow pipe

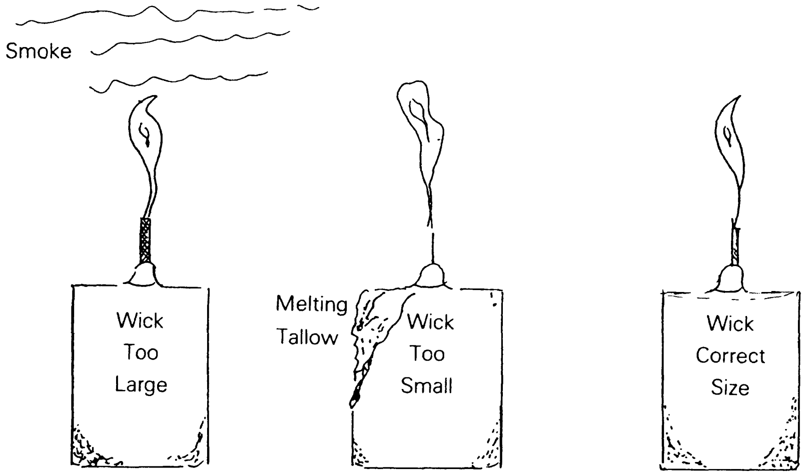


Figure 3.10. Correct and incorrect wick sizes

taper perpendicular to the candle. Experiment with different positions and study the results. See Figure 3.12.

To oxidize a sample for purposes of an assay or bead test, heat the sample with the portion of the yellow flame that is ¼ in. from the end of the blue flame. To reduce the same sample, heat it in the blue flame. See Figure 3.13. You should be able to produce a clean flame with the blue cone about 1 in. long. If the flame produced contains a yellow streak, trim or lower the wick.

If a flame cannot be produced that has a blue cone 1 in. long, the hole in the

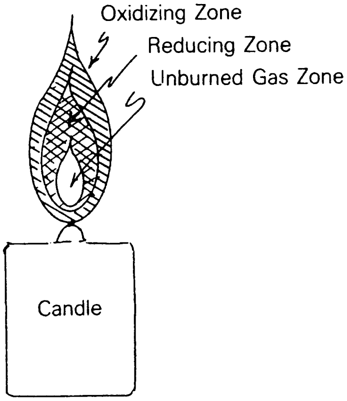


Figure 3.11. Candle flame zones

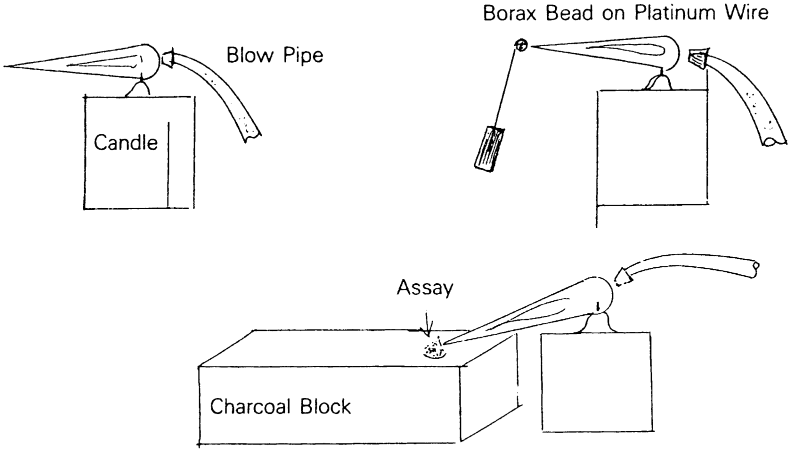


Figure 3.12. Normal blow pipe position

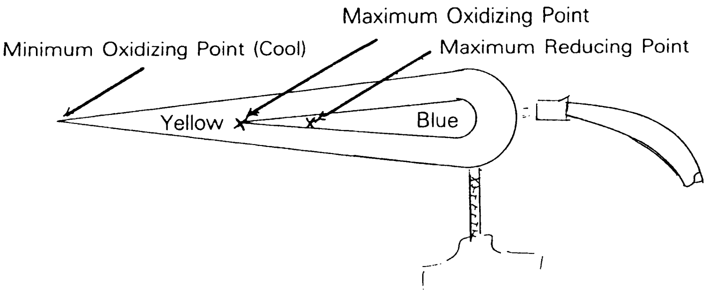


Figure 3.13. Oxidizing (yellow) and reducing (blue) portions of a flame

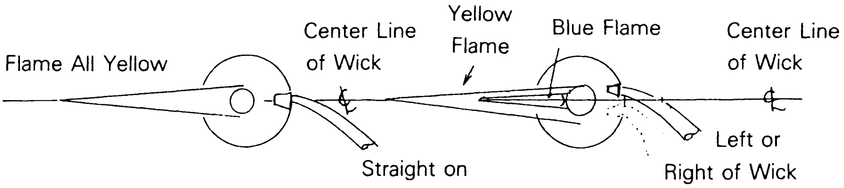


Figure 3.14. Controlling the flame

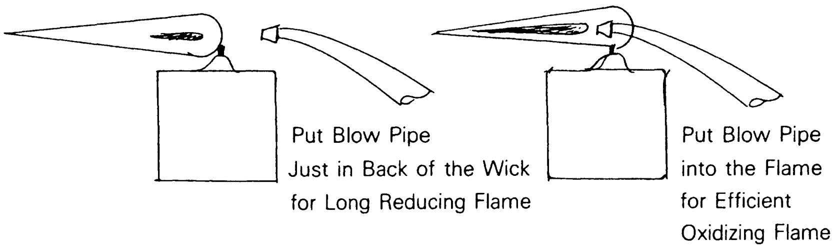


Figure 3.15. Producing a long reducing flame or an efficient oxidizing flame

tip of your blow pipe is too small. If the flame is excessively long and hisses, the hole in your blow pipe is too large.

Adjustments in the clarity and color of the flame can be accomplished by moving the blow pipe slightly to one side or the other of the wick; see Figure 3.14.

Another approach is to place the blow pipe just in back of the wick for a longer reducing flame, and directly into the flame for a more efficient oxidizing flame; see Figure 3.15.

Tests

Bead Test

The bead test is prepared by forming a bead of borax ($Na_2B_4O_7$), sodium metaphosphate ($NaPO_3$), or sodium carbonate (Na_2CO_3) in a small loop on the end of a platinum wire. See Figure 3.16. Borax ($Na_2B_4O_7 \cdot 10H_2O$) is a natural hydrated

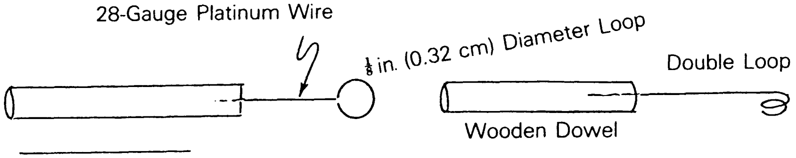


Figure 3.16. Platinum wire arrangements for bead tests

sodium borate. Sodium metaphosphate ($NaPO_3$) is also called Graham's salts, phosphorus salt, and sodium ammonium phosphate. Sodium carbonate ($Na_2CO_3{\cdot}H_2O$) has many forms, including soda ash, sal soda, and sodium bicarbonate.

A single loop for most tests is fine. A double loop is better for holding larger quantities and is useful when testing with sodium phosphate because this material is much more liquid than borax and is harder to form and keep on the wire. To form the bead, you heat the loop in the burner or with the blow pipe and dip the loop into (for example) powdered borax. You then fuse this material into a clear bead or globule and repeat the procedure until you have a good-sized clear, spherical bead formed in the loop. See Figure 3.17. The same procedure would be used to make a sodium metaphosphate bead or a sodium carbonate bead. When making a bead, take your time; simply make small additions, heat each until it stops bubbling, and then add more.

A straight wire can be moistened on your tongue and dipped into the powdered borax (cold), then heated. This will give you a miniature bead.

The principle behind bead tests is quite simple. Various compounds and oxides impart to the fused bead various colors that give clues to their identification. The glassmaker and the potter, with his glazes, impart a desired color by mixing various metallic compounds with the glass or glaze. Some compounds produce different colors, depending on whether the bead is hot or cold and whether they are under an oxidizing flame, a neutral flame, or a reducing flame. Other compounds consistently produce the same color regardless of variations in these factors.

Before being used in an actual test, the material to be tested is ground to a fine powder. The bead is then heated and lightly touched to the material under examination, picking up a very small portion; then it is heated under an oxidizing flame and observed hot and cold; and then it is heated under a reducing flame and observed hot and cold (for colors).

The biggest problem with bead tests is that the operator often picks up too much of the test sample on the bead. This can give you a bead that, for example, looks black but in reality is green. You only need an extremely small amount of material to color the bead; a speck of the sample is usually sufficient. It is wise to perform several bead tests on the same material to get a reliable indication of the exact colors being displayed on the bead.

Figure 3.17. Beads formed in a loop and on a straight wire

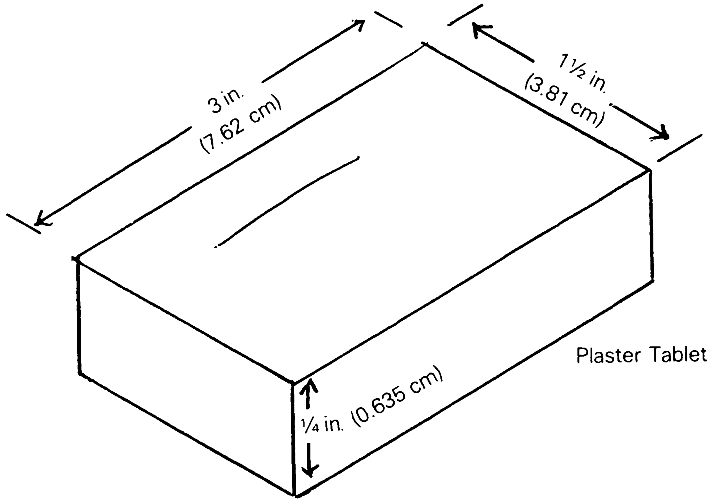


Figure 3.18. Plaster tablet for blow pipe tests

Plaster Tablets

Plaster of Paris tablets are extremely useful in helping to identify sublimates that could be misleading on the charcoal block or in closed or open tube tests. The procedure is to hold the plaster tablet above the test being made, so that the fumes form a sublimate on the tablet.

To make the tablets, clean a piece of plate glass and coat it very lightly with olive oil. Mix up some Plaster of Paris and spread it out so that it is about ¼ in. thick on the glass. When it starts to set (while still soft, but not runny), score or cut it up with a knife, as you would fudge (in 3 in. by ½ in. rectangles). When dry (set), it is easily removed from the glass. See Figure 3.18.

Open Tube Tests

Various tests are done in what is called an open tube. The open tube is a glass tube, open at both ends, about 5 in. long with an inside diameter of approximately ⅜ in. (9.5 mm). You can make them yourself from inexpensive glass chemical tubing sold by your chemical equipment supplier. The tube is bent on one end at an angle of about 60°, 2 in. from the end.

The material to be tested is placed inside, and the tube is held with a test tube holder in the Bunsen burner so that the flame can play up the steeply inclined long arm of the tube. This ensures a sufficient draft up the tube. Open tube tests are tests requiring oxidizing conditions. Sometimes, you have to blow at the lower end of the tube with the blow pipe to increase the draft. See Figure 3.19.

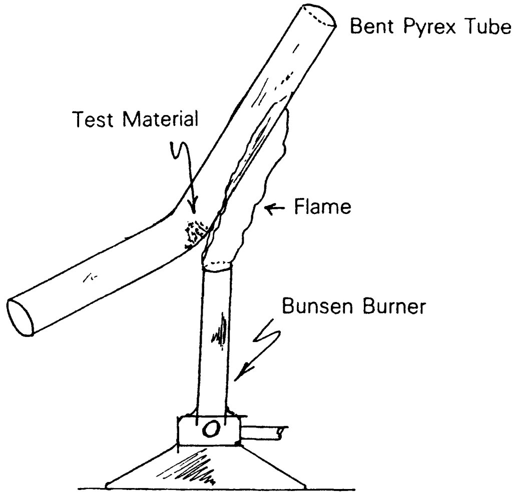


Figure 3.19. Open tube testing

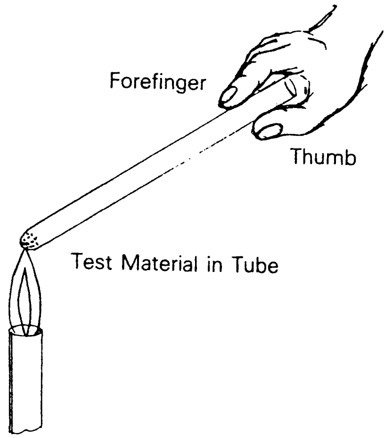


Figure 3.20. Closed tube testing

Closed Tube Tests

The closed tube is the same size and length as the open tube but is closed on one end and is not bent. An open tube can be closed by heating and rotating it in the burner. Tubing is usually purchased in 4-ft lengths; if heated and pulled apart in the length you wish, the tubes are easily closed.

The closed tube is used for making tests in which you wish to heat a sample with little oxidation. In the closed tube, the sample should not be ground into a fine powder but left in splinters (small fragments). If you try to test with fine powder, the powder adheres to the sides of the tube and interferes with sublimates. Indications discoverable with the closed tube include decrepitation, phosphorescence, fusion, and changes in form, color, and magnetism. In closed tube testing, you want to keep the open end cool by holding it in your fingers, with the tube almost horizontal and the closed end in the flame. See Figure 3.20.

Materials containing sulphur must be freed of sulphur by roasting (desulphurizing) on the charcoal block under a blow pipe in order to convert the material from a sulphur compound into an oxide. To do this, spread out the material thinly on the charcoal block and heat it with a small oxidizing flame from a considerable distance, never letting the material get any hotter than a dull red. See Figure 3.21.

Flame Color Tests

Flame color testing is simple and is based on the fact that some minerals, on ignition, impart a distinct color to the blow pipe flame or Bunsten burner flame.

On a tight loop of platinum wire, place your sample, or wet the wire and dip

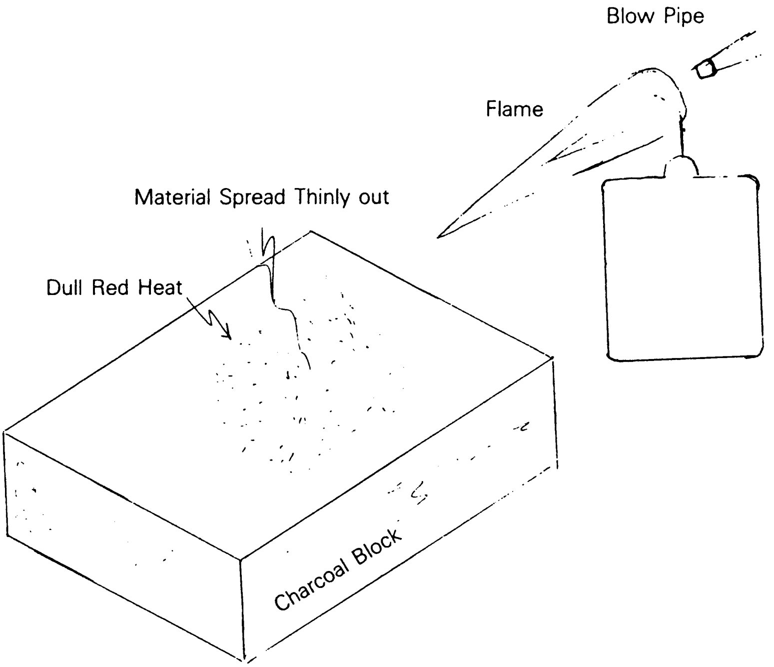


Figure 3.21. Roasting a sample with the blow pipe

it into the powdered material. Introduce it into the cool (unburning) area of the flame, then move upward slowly into the central part near the tip (the hottest point) and observe the flame color. Small slivers of material can be held in the flame with fine, platinum-tipped tweezers. See Figure 3.22.

Mixed flame colors can mislead you; for example, yellow and blue can appear as green. Consequently, some sort of light absorption filters are very helpful: blue and green glass or tinted plastic. An old but still valid method is to make what is called a Merwin flame color screen. Get a piece of transparent blue sheet plastic and another piece of transparent violet from your art supply dealer or graphic art supplier, cut a strip of each 6 in. long by 1½ in. wide, and overlap and glue them together at the bottom. This gives you three color divisions, which can be called blue, overlap, and violet. See Figure 3.23. You can make a similar screen of green and blue plastic.

In all of the identification tests discussed above, familiarity with the techniques and with the way the various results are supposed to look is essential to efficiency. You should practice with known materials so you know what to expect and how to interpret actual tests. You can purchase small lots of various oxides and so forth from chemical or ceramic supply houses. Use these to sharpen your procedure and

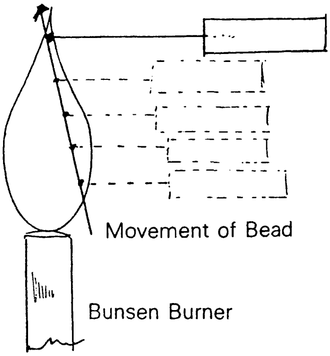


Figure 3.22. Flame color test

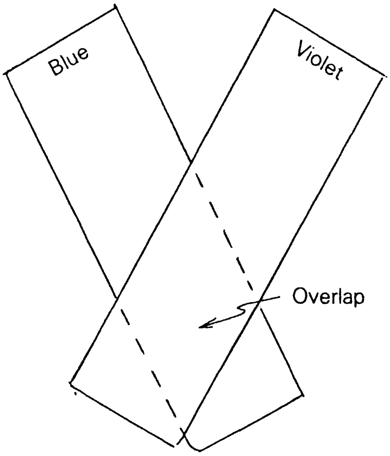


Figure 3.23. Flame color screen

familiarity with materials, and keep pure samples to use as standards from time to time for confirmation.

Equipment

In general, you should purchase equipment as needed and not try to get everything at once. Buy high-grade equipment: You are going to be using this testing equipment more often than anything else during familiarization, and even more when you proceed to the stage of actually extracting and refining. The list below will give you a good starting point.

1	test tube holder (wood or wire); see Figure 3.24
1	mouth blow pipe
1	set of watchmaker's tweezers
2	3-in. pieces of fine platinum wire (26 or 28 gauge)
1	test tube rack; see Figure 3.25
1	small hammer
1	small metal block (to use as an anvil)
1	Bunsen burner; see Figure 3.26
1	horseshoe permanent magnet
1	porcelain spot plate; see Figure 3.27
5	dropping bottles with glass stoppers (50 cc size); see Figure 3.28
1	set of 8 gold needles (4kt, 6kt, 8kt, 10kt, 12kt, 14kt, 18kt, and 20kt); see Figure 3.29

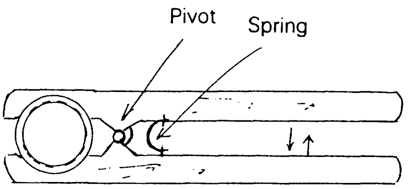


Figure 3.24. Wooden test tube holder (clothespin type)

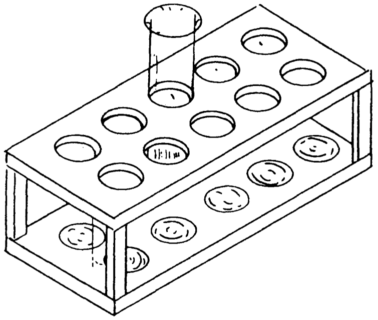


Figure 3.25. Test tube rack (wooden or plastic)

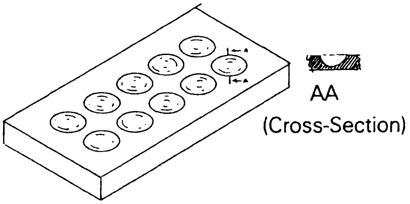


Figure 3.27. Glazed porcelain spot plate

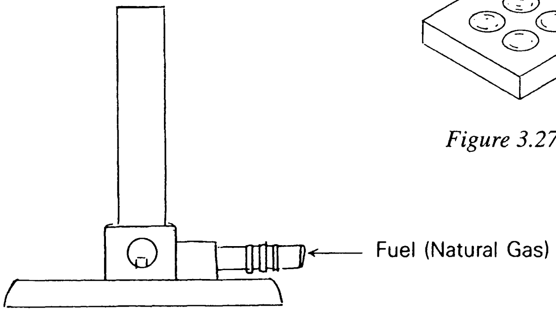


Figure 3.26. Bunsen burner

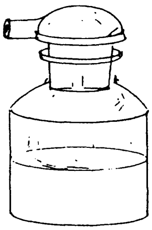


Figure 3.28. Dropping bottle

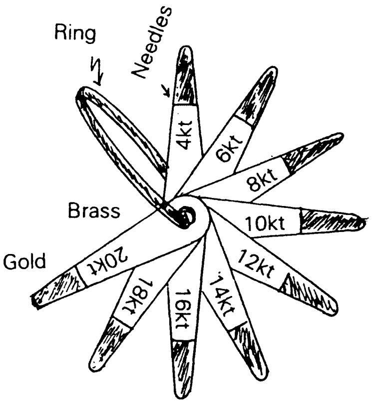


Figure 3.29. Gold testing needles

1	touchstone (fine-grained Arkansas whetstone)
1	plastic 1000 cc squeeze-type wash bottle, see Figure 3.30
1	5-in. glass funnel; see Figure 3.31
1	acid-proof rubber apron
1	pair of goggles
1	pair of rubber gloves
1	funnel support (wood or plastic—this you can make); see Figure 3.32
12	test tubes (20 mm × 150 mm size—about 13/16 in. × 4.9 in.; see Figure 3.33. (Test tubes much smaller than this are a nuisance to use and are apt to boil over or have their contents erupt.)
1	test tube brush; see Figure 3.34
2	large steel standard gold pans; see Figure 3.35
1	250-ml graduated glass marked off in ounces and milliliters; see Figure 3.36
4	dropping bottles (30 cc to 50 cc capacity) with glass touch rod; see Figure 3.37
4	porcelain-glazed evaporating dishes (75 mm top diameter, 70 ml capacity) (deep design); see Figure 3.38
1	cast-iron mortar and pestle (medium size); see Figure 3.39
1	steel Plattnor's diamond mortar with sleeve; see Figure 3.40
2	or 3 small Pyrex beakers (500 ml size—about 1 pint); see Figure 3.41
2	or 3 small Pyrex beakers [250 ml size—about ½ pint (liquid)]
4	or 5 glass stirring rods
1	glass or electric hot plate; see Figure 3.42

An electric hot plate with a magnetic stirrer-motor and adjustable heat control can be purchased from any chemical supply house. With this type of lab stove, a solution can be heated, stirred, or both, fast or slow, automatically.

The tops of these units are coated with glazed ceramic. They are easy to clean and the unit is not digested or oxidized away by the (sometimes) oxidizing environment to which it is subjected. This type of lab stove is expensive, but more economical in the long run, and actually costs you less if you take into account time saved and avoidance of replacement costs of cheap units. All you have to do is spend some time stirring with a glass rod to appreciate the convenience of this automatic unit. You can start it in a closed fume hood and let it do the rest.

The stirring is done by a Teflon-coated steel bar called a spin bar. The bar is placed in the beaker or flask containing the material to be heated or stirred. An

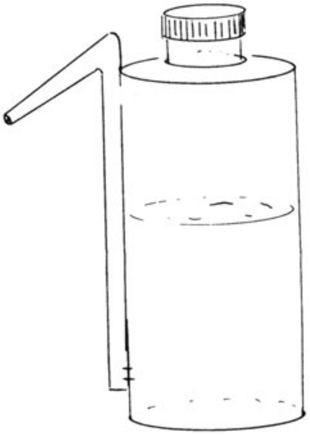


Figure 3.30. Plastic squeeze-type wash bottle (1000 cc)

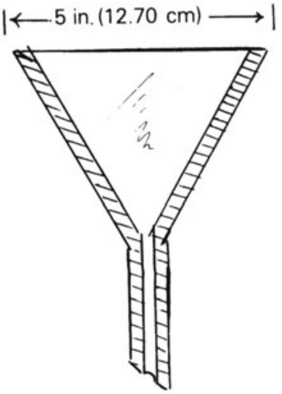


Figure 3.31. Five-inch glass funnel

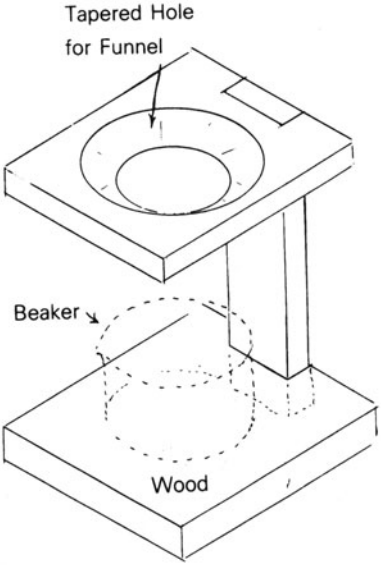


Figure 3.32. Homemade funnel support

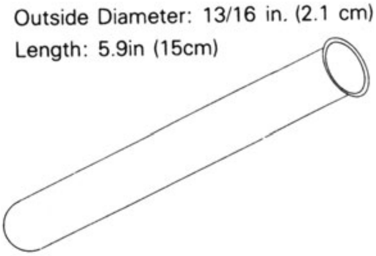


Figure 3.33. Test tube for general work

Figure 3.34. Test tube brush

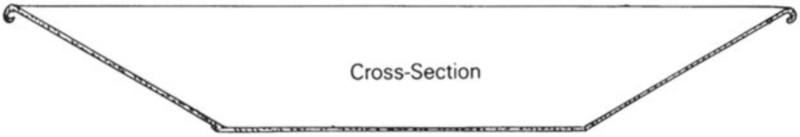


Figure 3.35. Steel gold pan

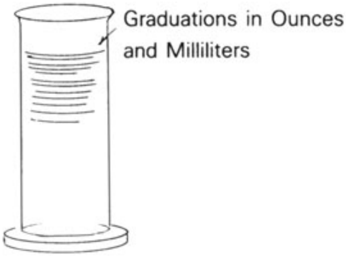


Figure 3.36. Glass graduate

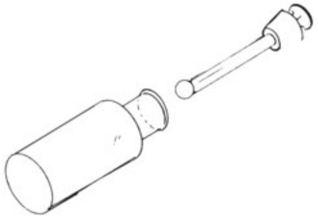


Figure 3.37. Dropping bottle with touch rod

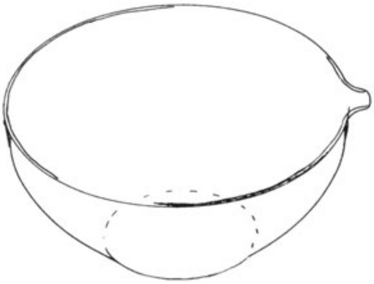


Figure 3.38. Porcelain evaporating dish

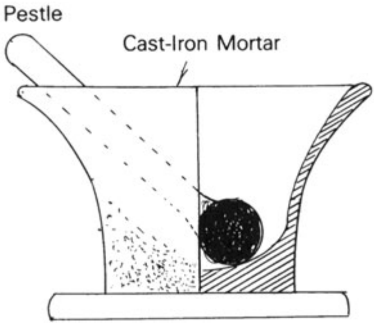


Figure 3.39. Cast-iron mortar and pestle

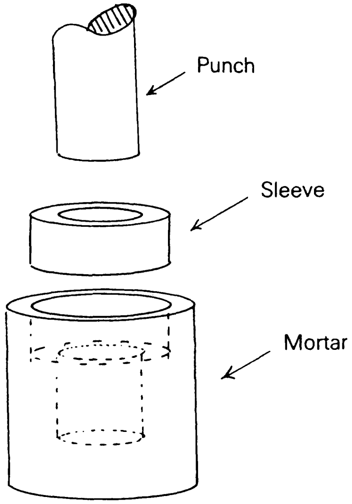


Figure 3.40. Plattnor's diamond mortar

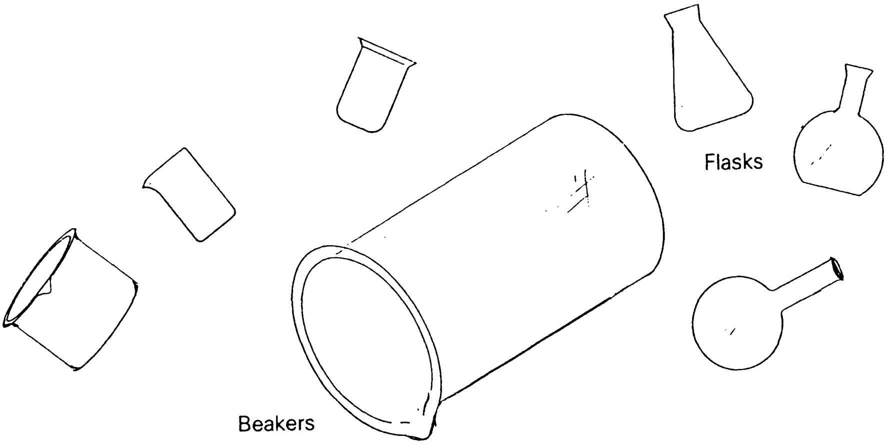


Figure 3.41. Pyrex beakers and flasks

electric motor with speed control inside the hot plate revolves a magnet which in turn revolves the stirrer (spin bar); see Figure 3.43.

Supplies and Reagents

Some supplies are perishable, such as charcoal blocks and filter papers. Other supplies and chemicals are consumed in various reactions and are classified as reagents.

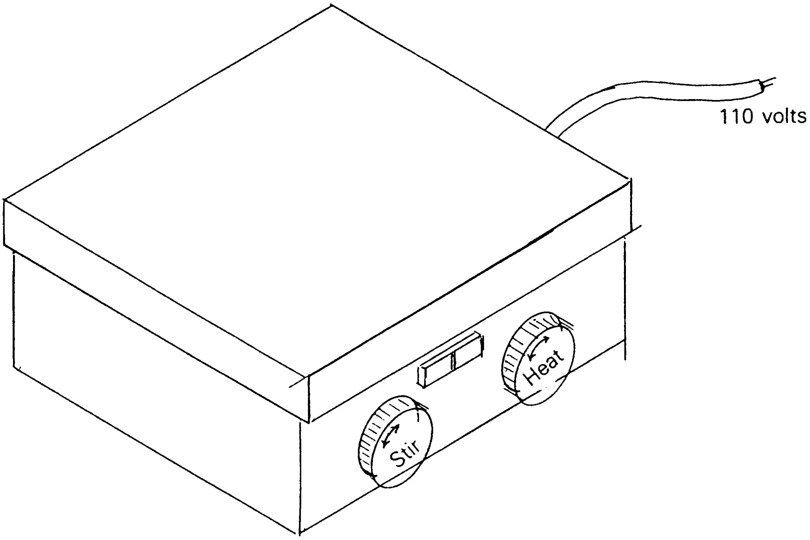


Figure 3.42. Hot plate with magnetic stirring device

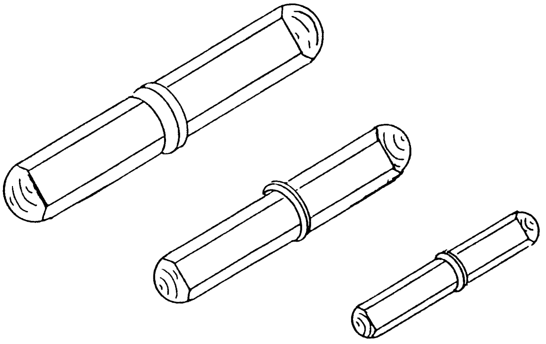


Figure 3.43. Magnetic spin bars

In very general terms, a reagent is a chemical substance that is used to produce or cause a chemical reaction. Some reagents are liquids, some dry materials, and some gases. The following list of reagents includes only what are normally called shelf reagents; these you should have on hand. Special reagents are made or purchased as needed. Other, more common reagents have a very short shelf life or generate gas and cannot be conveniently confined, and therefore are not suitable for premixture and storage on the shelf. Examples of these are stannous chloride solution and aqua regia. Test tubes can be bought in large or small quantities, depending on how fast you break them.

Supplies

1 or more packs 25-cm filter papers (medium porousness, quantitative)
1 set pH papers, with a range from 4 to 14 pH
Charcoal blocks for use with blow pipe
Plaster tablets (you make)
4 or 5, 4-ft lengths of glass lab tubing (9.54 mm—⅜ in.)

Dry Reagents

1 pound	sodium carbonate (Na_2CO_3) (sodium bicarbonate or common baking soda)
1 pound	borax ($Na_2B_4O_7 \cdot 10H_2O$) (hydrated sodium borate)
1 pound	salt of phosphorus (sodium ammonium)
1 pound	potassium chloride (KCl)
1 pound	ferric ferrocyanide $[Fe_4[Fe(CN)_6]_3]$ (note: this compound has a low toxicity)
1 pound	potassium bisulphate ($KHSO_4$)
1 pound	powdered fluorite (CaF_2)
1 ounce	granulated chemically pure tin (Sn)
1 pound	chemically pure granulated or mossy zinc (Zn)
1 pound	potassium nitrate (KNO_3) (niter, nitre, saltpeter)
1 pound	powdered galena (PbS)
2 pounds	plaster of Paris ($CaSO_4 \cdot 2H_2O$)
2 pounds	anhydrous soda ash (Na_2CO_3) (calcined sodium carbonate) ("anhydrous" means water-free)
2 pounds	crushed, lead-free flint glass
1 ounce	dimethylglyoxime or DMG (butane dioxime)
2 pounds	oxalic acid
1 pound	copperas ($FeSO_4 \cdot 7H_2O$) (ferrous sulphate) (contains no copper at all: the name is misleading)
1 pound	ammonium chloride (NH_4Cl) (sal ammoniac)
¼ pound	stannous chloride ($SnCl_2$) (tin salt)
1 pound	sulphur (flowers of sulphur)
1 pound	iodine-free table salt (NaCl) (sodium chloride)
1 pound	sodium hydroxide (NaOH)

(Several pennyweights 24kt gold (foil or fine granules)

Dry Fluxes

General Melting Flux (parts by volume)
  5 parts soda ash
  4 parts calcinated borax
  2 parts flint glass (lead-free)

Kobell Testing Flux (parts by volume)
  1 part potassium iodide

2 parts sulphur
1 part potassium bisulphate

Turner Testing Flux (parts by volume)
1 part powdered fluorite
3 parts potassium bisulphate

Liquid Reagents

Distilled water (H_2O)
Hydrochloric acid (HCl) (muriatic acid) (CP or reagent grade)
Sulphuric acid (H_2SO_4) (oil of vitriol)
Nitric acid (HNO_3) (aqua fortis)
Nitrohydrochloric acid (aqua regia) (do *not* attempt to store)

Acids

Acids are highly corrosive. They can cause severe burns and should be handled with extreme care. Never store acids near or around cyanides. Together, they produce very deadly hydrocyanic gas. If you get acid on your skin or in your eyes, flush with plenty of water; then neutralize with a safe base in solution (such as sodium bicarbonate in water).

When combining an acid with water, always add acid to water (and slowly); *never* the other way around. Water added to concentrated acid will cause the acid to react violently, spitting.

It is not often that you use an acid in the concentrated form in which it comes from the supplier; usually, you use it diluted to a 5 *N* molar solution. You should mix your acids in pint-sized quantities in acid bottles, labeling them clearly: hydrochloric acid 5 *N*, nitric acid 5 *N*, and sulphuric acid 5 *N*. Start out with 1 pint of each.

Hydrochloric acid, with a specific gravity of 1.20, if mixed with an equal volume of distilled water, will yield a solution just a wee bit stronger than a 5 *N* solution, which is fine. Nitric acid with a specific gravity of 1.42, if mixed with two volumes of distilled water, will be at a strength close to a 5 *N* solution. Sulphuric acid with a specific gravity of 1.84, if mixed with six volumes of distilled water, will yield about a 5 *N* solution.

Remember to add the acid to the water slowly, in small amounts, allowing the mix to cool down between additions of acid in order to prevent an excessive buildup of heat.

The specific gravities given below are those at which concentrated acids are sold by suppliers. Acids are usually sold by the pound. At 1.42 specific gravity, 1 gal of nitric acid weighs 11.36 lbs. At 1.84 specific gravity, 1 gal of sulphuric acid weighs 14.72 lbs. At 1.20 specific gravity, 1 gal of hydrochloric acid weighs 9.6 lbs.

In small quantities, acids are expensive; in large quantities, they are considerably cheaper, but more difficult to handle.

Aqua regia is called "royal water" because of its ability to dissolve gold and platinum, which are insoluble in any single acid. Nitrohydrochloric acid (aqua regia) is just what the name indicates: a mixture of nitric acid and hydrochloric acid. The most common proportions are (by volume) three parts hydrochloric acid and one part nitric acid. The two acids are combined and warmed slightly until they take on a dark reddish orange color. This is an extremely corrosive acid and is gasifying continuously—therefore, you should *not* cap up this compound in a bottle. Mix it as needed and in quantities no greater than needed to do the job at hand.

Bases

Ammonium hydroxide or aqua ammonia (NH_4OH) is simply ammonia gas (NH_2) dissolved in water. If you purchase the ammonium hydroxide at a specific gravity of 0.90 and add one volume of distilled water to one volume of it, you will have approximately a 5 N molar solution, which will neutralize an equal volume of any of the 5 N mole acids. This is a great help in speeding completion of reactions.

Ammonium molybdate (NH_4MoO_4) solution is made by dissolving a pennyweight (24 grains or 1/20 ounce) of ammonium molybdate crystals in about 30 cc of distilled water that has been made slightly alkaline (basic) with ammonium hydroxide (use your pH papers here). When ready to use, place a little of the solution in a test tube and add 5 N nitric acid, drop by drop. A precipitate will form. Continue to add nitric acid, drop by drop, until the precipitate goes back into solution (clears).

Potassium hydroxide (KOH) is also known as caustic potash. Buy 1 pint of the 45% reagent; it comes dry, in pellets, and you can keep them in a tight, well-stoppered bottle and dissolve them in a little water, as needed.

Cobalt nitrate [$Co(NO_3)_2$] solution is made by dissolving ⅛ teaspoon of $Co(NO_3)_2$ in ½ ounce of distilled water.

As your store of reagents grows and your understsanding of chemical reactions sharpens, you will find many uses other than testing for your reagents.

Work Area

If you do not provide for the removal of fumes, you are going to have to work outside and stay on the upwind side of any fumes. There are several work area arrangements that you can choose from, but never work with any chemicals in your house or living quarters, or in any area to which children or pets have access. The best system is a separately located outbuilding. You must have a washbasin (stainless steel), hot and cold water, and a means of getting rid of fumes.

The best way to get rid of fumes indoors is to use a glass-enclosed fume hood with positive exhaust system. Some people simply use a three-sided box

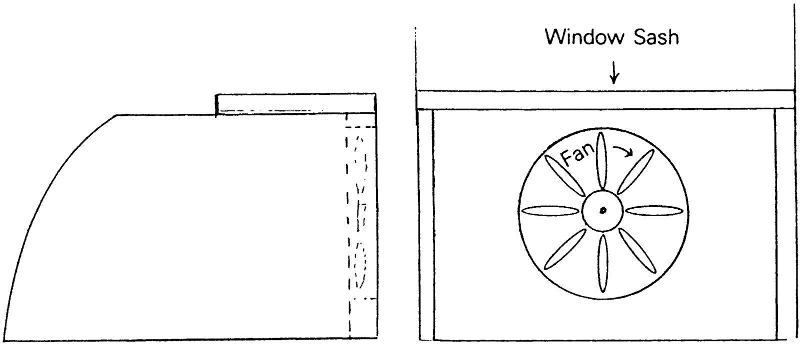


Figure 3.44. Small bench exhaust in window

arrangement with an exhaust fan. See Figure 3.44. However, with this arrangement, fumes being expelled go through the fan motor, which rapidly digests the fan. The preferred system is a totally enclosed lighted hood with a glass door that, when closed, is sealed with sponge rubber strips; the exhaust system operates indirectly. See Figure 3.45.

Some operations, regardless of how small, produce oxidizing, noxious, toxic, corrosive, suffocating fumes. Of course, the smaller the operation, the smaller the amount of fumes emitted. Under no circumstances, however, do you want to expose your other machinery and tools to corrosive vapors from your chemical operations. It is amazing, but if you were to place a water glass with a spoon of

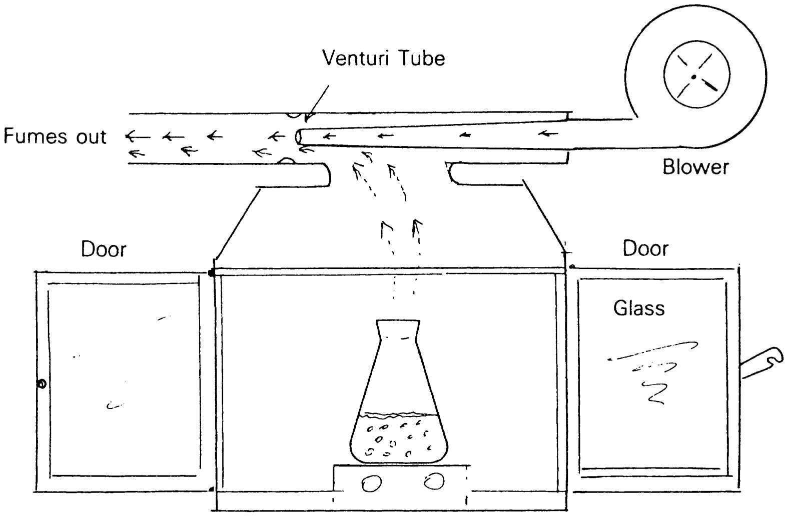


Figure 3.45. Enclosed fume hood

nitric acid in it in your workshop, and leave it overnight, the next day your tools and machinery would be covered with a nice coat of rust.

Your chemical equipment dealer will be happy to advise you on hoods, fume scrubbers, and lab furniture, to fit whatever size operation you intend to have.

Test Identifications

The tests given here are for detecting the presence of a particular element, not for making an assay—which is made to determine the amount per unit weight in the sample of the element identified by a test. Some of the tests here are miniature assays, extractive procedures, or refining procedures that you will recognize.

Testing with the blow pipe and with wet chemical methods covers hundreds of elements and compounds. Covered here are only the ones pertinent to the recovery and refining of precious metals, which include tests for base metals and elements that are often associated or combined with precious metals, and tests for salts and solutions that you have to be able to identify to make the picture complete.

The tests given here are not always the only ones you can use for a particular identification. There are many ways to test and many instruments to test with, such as spectrometer testing and atomic absorption.

Sublimates

Under ignition with the blow pipe on the charcoal block, sublimates usually form on the surface of the block in two areas—one near the test sample and one farther out from the test sample—with a distinct division between the two.

Cut a small groove about 1 in. from the edge of a charcoal block and place a few small granules of zinc in the groove. Heat the zinc in an oxidizing flame, gently at first, keeping the visible flame away from the test. Increase the temperature (by blowing harder), still not allowing the visible flame to come near or touch the test.

While heating, you should look for the following reactions and note them. First, decrepitation (bursting and cracking); Second, deflagration (burning and intense light); third, visible fumes; fourth, colors. Now stop the heat. The moment you discontinue the heat, you will note the following: odors, a change in the sample's color from its color under blast, and the color and position of the sublimate, if any. See Figure 3.46.

Now, using the blow pipe, subject the white sublimate [which is zinc oxide (ZnO)] to an intense hot flame in the oxidizing portion of the flame; it will not volatilize (go to fumes). Zinc oxide has a melting point of 1975°C.

Moisten another zinc sample with cobalt nitrate [$Co(NO_3)_2$] reagent solution. Repeat the test. This time, the sublimate appears green. This second test is a

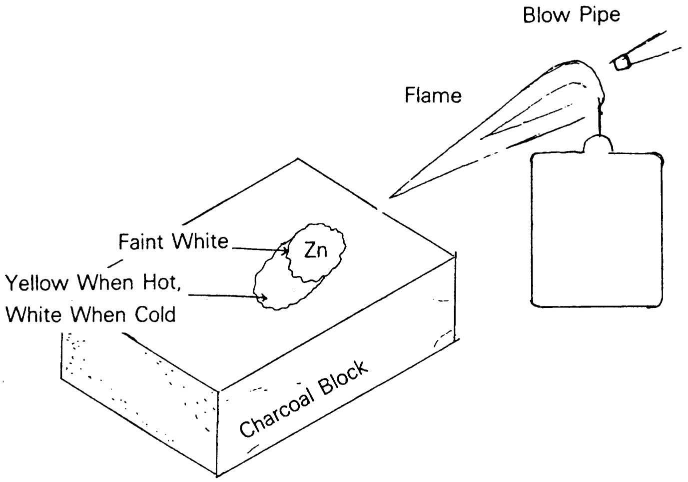


Figure 3.46. Zinc test under the blow pipe

confirming test: if the test material turns black, let it cool and check it to see if it is magnetic. Do not confuse ash with sublimate.

After oxidizing a test sample, subject it to strong heat in the reducing flame to see if you can produce globules of metal. Some metallic minerals are difficult to reduce from an oxidized state to a metallic state. You can make a very useful reducing flux by combining equal volumes of powdered borax, soda, and charcoal. Mix the test sample at a ratio of about three volumes of reducing flux to one volume of the sample material. You might have to dampen the ingredients to obtain a good mixture. Work it up into a small pellet; then heat it—at first lightly to dry it, so that the mixture will stick together, then intensely with a reducing flame for up to a minute—and reduction of metallics will occur. Some metallics reduce very easily under the reducing flame on the charcoal block, with no flux. Lead oxide is the easiest; try it for practice.

For ashes of burned photo or X-ray film, a great flux to use to check for silver values is one composed of 6 ounces of ground soda ash, 2 ounces of borax, and 2 ounces of sodium nitrate. This is a strongly oxidizing flux, getting oxygen from the sodium nitrate (saltpeter). Use it as you would the soda–borax–charcoal flux under an oxidizing flame. It is also useful for checking Au values in gold-bearing ashes. If copper or other easily oxidized minerals are present in the sample, they will not be reduced to metals with this flux, but will remain as or be converted to oxides.

If you are confused with a product of reduction on the charcoal block—with or without the borax–charcoal–soda flux—because it is a balled-up mess that gives no clue to its pedigree, grind it up in warm water in your cast-iron mortar. The water will dissolve the soda, and you can float off the charcoal. Whenever you resort to this procedure, when you remove the test from the charcoal block, you should remove and grind up a good portion of the charcoal that is under the test along with the test, to assure that you have everything from the original sample.

If you have succeeded in a reduction or partial reduction, you will find the metallics in the form of bright, flat scales on the end of the pestle and on the bottom of the mortar. Wash the metallics off onto a filter, drain and dry them, then transfer them to a small evaporating dish and do a chemical evaluation test for values identification. The following wet chemical testing should be done under the exhaust hood.

Add a few drops of nitric acid, enough to cover the metallics, warm the mixture, and add some additional water (a few drops). If the metallics go into solution, and a white precipitate falls, this is probably tin oxide (an insoluble oxide). Filter off the tin oxide (if found) and rinse it well with distilled water on the filter paper so that the excess liquid filters into the mother liquid. Then set aside the filter and its white precipitate to dry. Now drop a few drops of 5 *N* sulphuric acid (H_2SO_4), the reagent acid, into the mother liquid.

If the mother liquid drops a white precipitate, this is most likely lead nitrate. Filter it off, and set it aside to dry. Now, add a small pinch of table salt (sodium chloride) or a few drops of 5 *N* hydrochloric acid to the mother liquid (known as the filtrate). If silver is present, it will come down as a white curdy precipitate—silver chloride. Filter this off onto a filter paper, and let it dry.

You can check the silver chloride for positive identification in several ways. One way is to put a pinch of it in a test tube, cover with ammonium hydroxide, warm, and shake; if the white precipitate is silver chloride, it will go into solution, and, if you acidify the solution with nitric acid, it will reappear as the same white precipitate. Another method is to place a pinch of it in the sun or under a bright light; if it is silver chloride, it will go from white to light bluish to black in a short time (the principle behind photography). A third method is to mix it with a pinch of finely ground soda ash, dampen the mixture, shape it into a small pellet, and reduce it to metallic silver under the reducing flame on the charcoal block.

If the mother solution is green or blue-green, check for copper. If you add a pinch of ferrocyanide [$K_4Fe(CN)_6$] and copper is present, the copper will fall through the solution as a reddish brown precipitate that can be confirmed by reducing it to a copper bead on the charcoal block under the blow pipe.

Suppose now that the bright, flat, metallic particles that first appeared in the mortar failed to yield to the nitric acid after being heated for awhile (that is, would not go into solution). Pour the nitric solution into a test tube and test it for silver by adding table salt. If nothing appears, discard the solution. Next, make up a small amount of aqua regia (three parts hydrochloric acid to one part nitric acid) in a test tube, and warm the solution until it is a deep orange-red color. Cover the metallic flakes in an evaporating dish with the heated aqua regia and slowly, under gentle heat, stir the flakes around with a slender glass rod until the metallics are dissolved. Now boil the solution slowly until you have what looks like a thick reddish syrup. Without letting the liquid evaporate entirely, add a few drops of 5 *N* hydrochloric and boil the solution down again to a syrup-like consistency. Do this three times in order to dispel all the nitric acid from the aqua regia (this is important). Then, dilute the last thickened solution with two to three volumes of distilled water, and pour this solution into a small clean beaker, washing the evaporating dish clean with a wash bottle (this liquid also goes into the beaker).

Now you need to make two test solutions: stannous chloride and dimethylglyoxime (DMG).

Stannous chloride testing solution does not keep well, so you should make small amounts of it and always check them against a standard gold solution before using. Put a pennyweight of stannous chloride crystals in a 30-cc dropping bottle, and add a pennyweight or less of pure tin metal. Fill the dropping bottle about three-quarters full of distilled water, and then add 25–30 drops of hydrochloric acid. The small piece of tin metal that you added at the beginning of this procedure will dissolve slowly and help keep the solution working longer.

Dimethylglyoxime (DMG) testing solution lasts for years, although you might have to filter it once and a while. Dissolve 1 g of DMG by bringing it to a boil in 100 cc of distilled water (about 4 fluid ounces). Let this stand overnight, then filter it to remove any crystals or sediment. The clear, filtered solution is put into a clean dropping bottle and labeled "DMG test solution." You should get into the habit of labeling all containers clearly.

You should have on hand three standard solutions: one each for gold, platinum, and palladium. These solutions are used to check your test solutions (reagents) and to compare or police your tests.

To make the gold standard solution, dissolve 2 grains (troy weight) of pure gold in a few drops of aqua regia in a small evaporating dish. Heat the solution gently until it is almost dry. Wash this off into a 2-ounce dropping bottle, then fill the bottle with distilled water up to the 2-ounce mark. Label the gold standard "2 grains troy Au in 2 oz. H_2O." Follow the same procedure with 2 grains (troy weight) of pure platinum, labeling the platinum standard "2 grains troy Pt in 2 oz. H_2O," and likewise with 2 grains of pure palladium.

Now you are ready to go back to the small beaker in which the unknown metallic flakes are in solution and identify them. Place a drop or two of solution from the small beaker into a cavity of a spot plate. (You can use a blotter or filter paper in lieu of a spot plate.) Next to this drop, place a drop of the gold standard. Now, to each drop, add a drop of stannous test solution. The gold standard at once goes from deep purple to black, a positive gold indication. If the unknown metal in your solution is gold, both the gold standard solution and your unknown solution will look exactly alike after the stannous test is added to them.

If, instead, the unknown turns a pale yellow, add another drop of stannous test solution; if it then changes to a deep yellow or brown, the metal in solution is probably a combination of platinum and iridium.

If, when adding a drop of stannous test solution to the unknown metal solution, you get a yellowish platinum indication, let it sit for a few minutes; if there is palladium in the solution, the spot test will turn blue-green, which is a characteristic of palladium.

Once again, practicing ahead of time with your three standards and your stannous chloride test solution will enable you to identify colors, reactions, and elements when you are working with unknowns.

Many times, there is more than one metal in a solution, which leads to confusing test results. Experiment with one drop of gold standard mixed with one drop of platinum standard. Check this with the stannous test and the DMG test. Try the same things with platinum and palladium together, with gold and palladium together, and with all three together. As you become knowledgeable with these and other tests, you will know how to change directions in your testing to get a positive identification.

If you were to come up with a confusing test result that indicated gold but you also wished to confirm the presence or absence of platinum, you would simply add a reagent to your solution to precipitate the gold values out of the solution, leaving a solution that you could check for platinum by the spot test. Then you would be ready to remove the platinum with a reagent. Add a copperas (iron sulphide) solution to an acid solution of gold, and the gold is precipitated as a brown powder. Filter off the gold and add ammonium chloride solution to the filtrate, and the platinum (if any) will precipitate as an orange powder (platinum ammonium chloride or ammonium chloroplatinate).

The art of testing is usually the basis for deciding what methods of extraction and of refining are best suited for a particular primary or secondary material.

Often, when testing for a particular value, you discover the presence of another value that constitutes a much higher percentage of the material (thus making it commercially more valuable) than the value for which you were testing. This could cause you to go after the new value as your primary objective and the original value as a by-product. There are countless cases in which tons of high-grade silver values went to the dump because someone was trying so single-mindedly to recover the gold values that he did not bother to check for silver. How would you like to be chasing a few ounces per ton of gold, only to find too late that you were in the middle of a high-grade copper deposit, or a smidgen of platinum in the midst of tons of nickel.

The example of the wet chemical test just given illustrates how simple it all is. You can have several different metals or nonmetals in a common solution and, by various treatments and reagents, selectively precipitate each out of the solution—sometimes one by one and other times in groups that can then themselves be treated for further separations singly or in new groups.

The various results of testing reveal what you have and in what combination and state. Once you have established this, you can decide which future method will give you the best yield at the least cost. The reason that several different methods of testing are given in this volume is simple: The more clues collected by subjecting an unknown to various methods of testing, the more positive is the resulting identification.

It is common in testing to call the material tested the assay, but this terminology is incorrect: Most tests are for the presence of a metal, not for the amount of it. An assay gives you the amount of an element or value as a percentage weight—grams per liter, ounces per ton, or pennyweight per troy ounce. To prevent confusion, however, I will go along with common usage and call the material being tested the assay.

Sublimates Produced on the Charcoal Block under the Blow Pipe

Here, again, you should subject as many known compounds (standards)—oxides, chlorides, and so forth—to sublimate tests as possible, in order to sharpen your eye to exactly what the test and its various results look like. You can observe the results of sublimate testing for substances not described below by testing knowns of those substances. See Figure 3.47.

Arsenic trioxide (AsO_3). The sublimate is mostly formed far from the assay and is white to grayish in color. Near the assay, it is white and very volatile. Arsenic compounds usually give off a strong garlic-like odor when heated.

Tellurium as an oxide (TeO) or as a free metal (Te). Near the assay, these are white and volatile; away from the assay, they are gray or brownish. Under a reducing flame, tellurium volatilizes, coloring the flame a pale green.

Antimony as an oxide (Sb_2O_3 or SbO_4). Near the assay these give off dense white fumes. Away from the assay, their color is bluish.

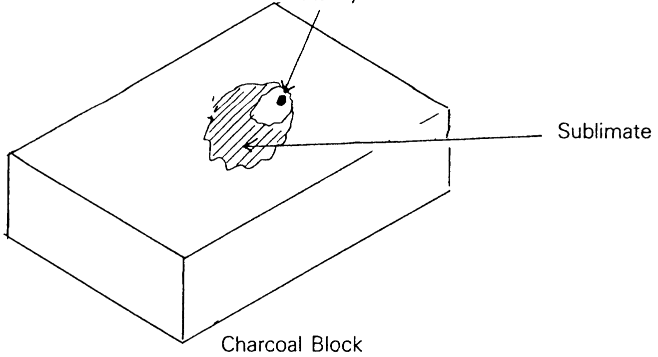


Figure 3.47. Sublimate on charcoal block

Various chlorides and alkalis, such as chlorides of copper (Cu), lead (Pb), mercury (Hg), and ammonium (NH_4). Their color near the test is white; away from test, white to bluish.

Tin dioxide (SnO_2). Near the assay, when hot, the sublimate is pale yellow, it is slightly less yellow when cold. Tin will not volatilize under the oxidizing flame. If tin dioxide is moistened with cobalt nitrate ($CoNO_3$), the sublimate is bluish green under the blow pipe.

Molybdenum trioxide (MoO_3). Near the assay, the sublimate is pale yellow, whether hot or cold, and volatilizes under an oxidizing flame. Away from the assay, the sublimate is bluish. When touched with a reducing flame, the sublimate is azure blue but copper-red near the test [a molybdenum dioxide (MoO_2) sublimiate].

Zinc oxide (ZnO). Near the assay, the sublimate is canary yellow when hot, whitish when cold. The sublimate will not volatilize under an oxidizing flame. Moistened with cobalt nitrate ($CoNO_3$), the sublimate is green.

Lead as an oxide (PbO), sulphite ($PbSO_3$), or sulphate ($PbSO_4$). Near the assay, these are bright yellow when hot and light yellow when cold. The sublimate will volatilize under an oxidizing flame or a reducing flame. Away from the assay, their color is faint white, and they will volatilize under an oxidizing flame or reducing flame. When lead oxide (PbO) is heated on the charcoal block with some Kobell flux, it forms a volatile yellowish green sublimate around the reduced metallic beads of lead.

Bismuth as an oxide (Bi_2O_3). Near the assay, this forms a sublimate that is a dark orange-yellow when hot, and a lighter orange-yellow when cold; it volatilizes under an oxidizing flame or a reducing flame. Away from the assay, the sublimate is greenish white. When fused with Kobell flux under an oxidizing flame on the charcoal block, it forms a sublimate that is yellow with a brilliant red fringe.

Cadmium oxide (CdO). Near the assay, the sublimate is black to brown and volatilizes under an oxidizing or a reducing flame. Away from the assay, the sublimate is yellow and the sublimate, if thin, is iridescent.

Gold (Au) mixed (alloyed by nature) with lead (Pb) and antimony (Sb). The sublimate near the assay is reddish to deep lilac. If you subject gold alone to long, intense ignition under the blow pipe on the charcoal block, you get a slight brownish sublimate.

Selenium as a white oxide (SeO_2) and as a red free metal (Se). Near the assay, the sublimate has a faint metallic luster and volatilizes easily; away from the assay, the sublimate is white, tinged with red. The sublimate under a reducing flame colors azure blue, and the odor is radish-like.

Iodides and Iodide Sublimates

Iodides are binary compounds of iodine and another, more electropositive atom or group. Silver iodide (Agl), as used in medicine and photography, and copper iodide or cuprous iodide (CuI), which is the source of the iodine in table salt, are examples.

An unknown sample or mineral can be ground and mixed with a little Kobell dry flux; then, when the mixture becomes fused, volatile iodides will form near the end of a plaster tablet held over it. The sublimate's reaction and color give clues to the unknown metallic element in the assay. If, after the unknown sample is ground, mixed with the Kobell flux (which is a sulphurous potassium iodide), and fused on a plaster tablet under the blow pipe, the sublimate that forms is scarlet with yellow, this would indicate that the unknown metallic element is lead. In each case, the Kobell flux should be used for checking iodide sublimates.

Lead as an iodide (PbI_2). On plaster, the sublimate is chrome yellow and volatilizes; on charcoal, it is basically the same.

Arsenic as an iodide (AsI_3). On plaster, the sublimate is yellow to orange and very volatile; on charcoal, it is faint yellow.

Antimony as an iodide (SbI_3). On plaster, the sublimate is orange to red. When subjected to strong ammonia fumes, it disappears. See Figure 3.48. On charcoal, the sublimate is pale yellow.

Mercury as an iodide (HgI). On plaster, heated moderately, the sublimate is scarlet with yellow; if heated strongly, it changes color to dull yellow and black. On charcoal, the sublimate is faint yellow.

Selenium as an iodide (SeI_4). On plaster, the sublimate is a reddish brown or scarlet; the sublimate shows no color on charcoal.

Bismuth as an iodide (BiI_3). On plaster, the sublimate is chocolate brown with underlying scarlet. When subjected to ammonia fumes, the sublimate turns orange and then cherry red. On charcoal, the sublimate is bright red away from the assay and yellow close to the assay.

Tellurium as an iodide (TeI_4). On plaster, the sublimate is purplish brown with a dark border; the sublimate shows no color on charcoal.

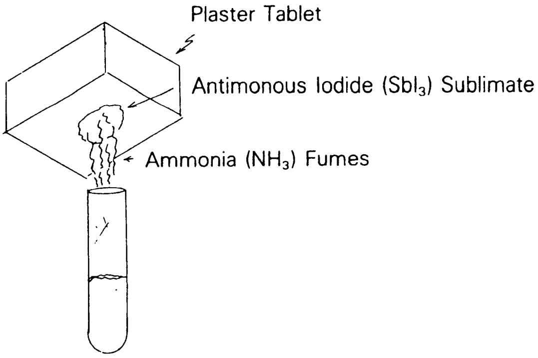


Figure 3.48. Testing sublimate on plaster tablet with ammonia fumes

Molybdenum as an iodide (MoI_4). On plaster, the sublimate is a beautiful deep ultramarine blue; it shows no color on the charcoal.

Sublimates in Closed Tubes

In the following descriptions, the term "cold" refers to the end of the tube that is cooled by being held between the tester's thumb and forefinger, and the term "hot" to the closed end that is in the flame. See Figure 3.49.

Lead chloride ($PbCl_2$). The sublimate is a white solid, hot or cold.

Antimony as a chloride ($SbCl_3$) or an oxide (Sb_2O_3). The sublimate is a white solid, hot or cold.

Ammonium as a salt (NH_4). The sublimate is a white solid, hot or cold.

Mercury (Hg). This element volatilizes rapidly at the hot end. The mercury fumes then condense at the cold end of the tube to form grayish metallic (pure mercury) globules, which can be united with a paper or rubber policeman.

Tellurium as an oxide (TeO_2). Tellurium oxide forms a pale yellow to colorless liquid when hot that does not volatilize easily with additional heat; at the cold end, colorless to white globules are formed.

Sulphur (S). Sulphur, when hot, melts to form a yellow to red liquid that volatilizes easily to form, on the cold end, a small quantity of pale yellow crystalline solids. This test is valid for most compounds as a check for the

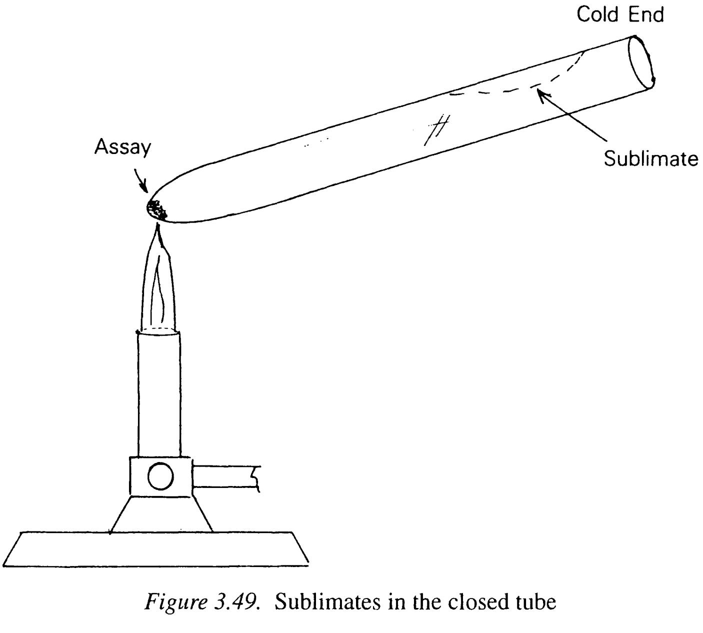


Figure 3.49. Sublimates in the closed tube

presence of sulphur. The test, when positive, is usually accompanied by the pungent odor of sulphur dioxide.

Arsenic as a sulphide (AsS) or as an oxide (As_2O_3). Either compound forms a dark red liquid when hot, and is easily volatilized to a reddish yellow solid that is transparent on the cold end.

Antimony as an oxidized sulphide (Sb_2S_2O). This compound forms a black solid, difficult to volatilize, on the hot end. The sublimate is reddish brown on the cold end.

Arsenic (As). On the heated end, arsenic forms a brilliant black (or sometimes gray) crystalline solid, hot or cold. If you break off the tip of the closed end and heat the black sublimate, you will smell the characteristic garlic-like odor.

Mercury as a sulphide (HgS). This compound produces a brilliant black solid, hot or cold. This sublimate, when rubbed, becomes a red powder.

Tellurium (Te). This element usually forms fusible black globules in the tube when heated, and these can then be checked as tellurides.

Selenium (Se). Hot or cold, when heated in the closed tube, this element produces easily fusible black globules; the smallest show a deep red color in transmitted light, and some white crystalline selenium dioxide (SeO_2) is often in evidence.

Sublimates in Open Tubes

In open tube testing, you should use only a very small amount of the material to be tested, so as not to restrict the flow (draft) of air through the tube. Look for your indicator clue as shown by the dotted line in Figure 3.50.

Arsenic as an oxide (As_2O_3). This compound forms a white crystalline sublimate that volatilizes easily.

Selenium as an oxide (SeO_2). This compound forms a white crystalline sublimate, sometimes mixed with fine dots of red selenium.

Antimony as an oxide (Sb_2O_3). This compound produces a white crystalline sublimate that forms in octahedrons and prisms.

Lead as a sulphate ($PbSO_4$). This compound produces a white, nonvolatile, unfusible sublimate that forms largely on the low side of the tube.

Tellurium as an oxide (TeO_2). The sublimate of this compound, when hot, consists of pale yellow globules difficult to volatilize. When cold, the sublimate consists of white to colorless globules.

Molybdenum as an oxide (MoO_3). The sublimate of this compound is pale yellow when hot and white when cold. When heated to a red heat, it will fuse; on continued heating, it will volatilize.

Mercury (Hg). The sublimate of mercury heated in an open tube is the same as that of mercury heated in a closed tube. See the closed tube test for mercury on page xxx.

Selenium (Se). The sublimate of this element is red and volatile.

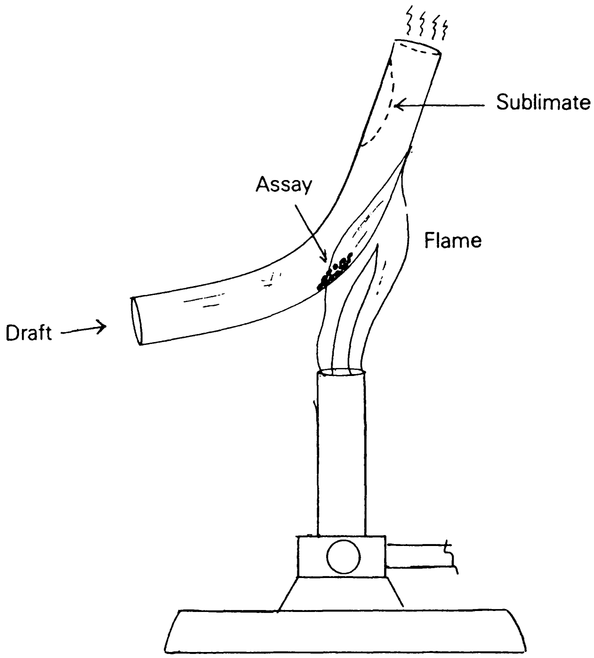


Figure 3.50. Sublimates in the open tube

NOTE: For each of the following substances, you must heat the tube above the assay first, and then more directly below the assay in order to get a classifiable sublimate.

Sulphur (S). The sublimate of this element is yellow to orange and easily volatilized.

Arsenic as a sulphide (AsS). The sublimate of this compound is yellow to orange and easily volatilized.

Antimony as an oxidized sulphide (Sb_2S_2O). The sublimate of this compound is black when hot and brown when cold; it is difficult to volatilize.

Arsenic (As). The sublimate of this element is a brilliant black and easily volatilized.

Mercury as a sulphide (HgS). The sublimate of this compound is a brilliant black and easily volatilized.

Flame Color Tests

With the Merwin screen, there are three color splits. In the descriptions below, the blue one will be called "A," the overlap "B," and the violet one "C." The first color given will be the color of the flame as seen with the unaided eye. See Figure 3.22 and flame test description page xxx.

Arsenic (As). The flame appears pale blue and is accompanied by a garlic-like odor.

Boron (B). The flame appears yellowish green; "A" is green; "B" and "C" are pale green.

Calcium (Ca.). The flame appears yellowish orange-red; "A" is greenish yellow, "B" is faint green, and "C" is pale crimson.

Barium (Ba). The flame appears yellowish green; "A" is green; "B" and "C" are pale green.

Copper as an oxide (CuO). The flame appears emerald green; if touched with (wet) hydrochloric acid, it produces a blue flame tinged with green.

Copper as a chloride salt ($CuCl_2$). The flame appears azure blue with an outer fringe of emerald green; "A" is bright green, "B" is pale green, and "C" is blue with a green outer fringe.

Lithium (Li). The flame appears crimson red; "A" and "B" show no color (they are invisible); "C" is crimson.

Manganese as a chloride salt (MnCl). The flame appears yellowish green; "A" is emerald, "B" is pale bluish green, and "C" is pale lavender.

Molybdenum (Mo) as an oxide or a sulphide. The flame appears pale yellow-green.

Sodium (Na). The flame appears very intense and yellow, but invisible through the color screen.

Phosphorus (P). The flame appears pale bluish green; "A" is green, "B" is pale green, and "C" is light violet-red.

Strontium (Sr). The flame appears crimson red; "A" and "B" are invisible; "C" is crimson.

Selenium (Se). The flame appears indigo blue and is accompanied by a radish-like odor.

Tellurium (Te). The flame appears pale green.

Lead (Pb). The flame appears a pale azure blue with a green tinge in the outer part of the flame.

Borax Bead Test

The descriptions below are of the colors imparted to borax beads by various metallic oxides under the blow pipe. If a substance to be assayed is not an oxide, it must be made so—by being roasted to remove sulphides—in order for the borax bead test to work.

Oxides of silicon (Si), aluminum (Al), and tin (Sn) add no color to borax beads.

Oxides of calcium (Ca), strontium (Sr), magnesium (Mg), zinc (Zn), zirconium (Zr), and niobium (Nb) [also known as columbium (Cb)] add little or no color to borax beads. At best, you might get an opaque whitish color.

Oxides of lead (Pb), antimony (Sb), and cadmium (Cd) add only a pale yellow color to borax beads when heated with an oxidizing flame or a reducing flame.

An oxide of titanium (Ti) adds a pale yellow color to a borax bead when heated with an oxidizing flame; this becomes practically colorless when the bead is cooled. When heated with a reducing flame, a borax bead becomes gray, and turns brownish violet when cooled.

An oxide of tungsten (W), when heated with an oxidizing flame, adds a pale yellow color to a borax bead; this becomes colorless to whitish when the bead is cooled. When heated with a reducing flame, a borax bead becomes yellow and turns yellow to yellow-brown when cooled.

An oxide of molybdenum (Mo), when heated with an oxidizing flame, adds a pale yellow color to a borax bead; this becomes colorless when the bead is cooled. When heated with a reducing flame, a borax bead becomes brown, and it remains brown when cooled.

An oxide of bismuth (Bi), when heated with an oxidizing flame, adds a pale yellow color to a borax bead; this becomes colorless when the bead is cooled. When heated with a reducing flame, a borax bead becomes brown, and it remains brown when cooled.

An oxide of uranium (U), when heated with an oxidizing flame, adds a yellow to orange color to a borax bead; this becomes almost colorless when the bead is cooled. When heated with a reducing flame, a borax bead becomes pale green, and turns almost colorless when cooled.

An oxide of chromium (Cr), when heated with an oxidizing flame adds a yellow-orange color to a borax bead; this becomes yellow-green when the bead is cooled. When heated with a reducing flame, a borax bead becomes green, and it remains green when cooled.

An oxide of vanadium (V), when heated with an oxidizing flame, adds a yellow color to a borax bead; this becomes yellow-green when the bead is cooled. When heated with a reducing flame, a borax bead becomes dirty green, but turns a nice clear green when cooled.

An oxide of iron (Fe), when heated with an oxidizing flame, adds a yellow to orange color to a borax bead; this becomes yellow when the bead cools. When heated with a reducing flame, a borax bead becomes bottle green, and turns light green when cooled.

An oxide of copper (Cu), when heated with an oxidizing flame, adds a blue color to a borax bead; this becomes light green to colorless when the bead cools. When heated with a reducing flame, a borax bead remains colorless or turns light green, and then turns opaque red when cooled.

An oxide of cobalt (Co), when heated by either an oxidizing or a reducing flame, and whether hot or cold, imparts to the bead a beautiful cobalt blue color.

An oxide of nickel (Ni), when heated with an oxidizing flame, adds a violet color to a borax bead; this becomes reddish brown when the bead is cooled.

When heated with a reducing flame, a borax bead becomes opaque gray and it remains opaque gray when cooled.

An oxide of manganese (Mn), when heated with an oxidizing flame, adds a violet color to a borax bead; this becomes reddish violet when the bead is cooled. When heated with a reducing flame, a borax bead remains colorless, both hot and cold.

Sodium Metaphosphate Bead Reactions

Oxides of calcium (Ca), strontium (Sr), barium (Ba), magnesium (Mg), zinc (Zn), aluminum (Al), zirconium (Zr), tin (Sn), and silicon (Si) give no coloration to metaphosphate beads, under any conditions.

An oxide of cadmium (Cd), when heated with either an oxidizing or a reducing flame, adds only a pale yellow color to a metaphosphate bead.

Oxides of lead (Pb), antimony (Sb), and bismuth (Bi) when heated make a metaphosphate bead gray to colorless.

NOTE: The descriptions below divide metaphosphate bead colors according to two factors: type of flame used (oxidizing or reducing) and temperature of the bead (hot or cold).

An oxide of niobium (Nb) [also known as columbium (Cb)]. Oxidizing flame: hot, yellow; cold, colorless. Reducing flame: hot, brown; cold, brown.

An oxide of tungsten (W). Oxidizing flame: hot, pale yellow; cold, colorless. Reducing flame: hot, dirty blue; cold, fine blue.

An oxide of titanium (Ti). Oxidizing flame: hot, pale yellow; cold, colorless. Reducing flame: hot, yellow; cold, violet.

An oxide of iron (Fe). Oxidizing flame: hot, yellow; cold, colorless. Reducing flame: hot, yellow-green; cold, colorless.

An oxide of uranium (U). Oxidizing flame: hot, yellow; cold, greenish yellow. Reducing flame: hot, pale green; cold, fine green.

An oxide of molybdenum (Mo). Oxidizing flame: hot, yellow-green; cold, colorless. Reducing flame: hot, dirty green; cold, clear green.

An oxide of nickel (Ni). Oxidizing flame: hot, red or reddish brown; cold, yellow or yellow-brown. Reducing flame: hot, red or reddish brown; cold, yellow or yellow-brown.

An oxide of copper (Cu). Oxidizing flame: hot, green; cold, pale blue. Reducing flame: hot, pale yellow-green; cold, blue or colorless or bright red.

An oxide of chromium (Cr). Oxidizing flame: hot, green; cold, green. Reducing flame: hot, green; cold, somewhat cleared-up green.

An oxide of cobalt (Co). Oxidizing flame: hot, cobalt blue; cold, cobalt blue. Reducing flame: hot, cobalt blue; cold, cobalt blue.

An oxide of manganese (Mn). Oxidizing flame: hot, violet; cold, colorless. Reducing flame: hot, colorless; cold, colorless.

Element-by-Element Identifications

The following portion of this chapter lists metallic elements, from aluminum to zinc, and offers some additional ways of identifying each, with some references to the blow pipe and bead tests. The streak test to which I sometimes refer in this section is simply a check of the color of the mark made on a clean, white, hard Arkansas whetstone, or on unglazed porcelain, or on a fine-cut file by the substance in question.

Aluminum (Al)

Specific gravity—2.70. Principal ore; bauxite (hydrous aluminum oxide), a non-crystalline, earthy, white to reddish mineral, massive or in grains.

Bauxite looks like clay. When rubbed between the thumb and forefinger, it is reduced to a fine powder (clay will not powder in this manner). Grind a dry sample in a small mortar. Bauxite will stick to the sides and bottom of the mortar (dry clay will not). Bauxite will not scratch glass (clay will). It is not gritty between the teeth. It will not fuse under the blow pipe, and it is insoluble in acids.

Place a sample of your assay on a charcoal block and apply one drop of cobalt nitrate solution (⅛ teaspoon of cobalt nitrate crystals dissolved in ½ ounce of water). Heat it strongly in the blue (reducing) flame with a blow pipe; if the assay turns blue, this indicates aluminum. To rule out zinc, test for zinc; if the zinc test is negative, then the assay is bauxite.

Aluminum in its metallic state dissolves in sodium hydroxide solution (lye), with effervescence producing hydrogen gas and a precipitate of aluminum oxide. Place some strong sodium hydroxide solution in a shallow evaporating dish and drop in it a small sample of the aluminum. The reaction, if the metal is aluminum, will generate copious bubbles, and if you hold a lighted match close to the solution's surface, the hydrogen will ignite with a popping noise and a miniature flash of light. Crystalline Drano is dry sodium hydroxide mixed with aluminum flakes, and this is the action it produces when wet. Considerable heat is also generated by this reaction.

Antimony (Sb)

Specific gravity—6.62. Principal ore: stibnite (Sb_2S_3), slender prismatic crystals with a metallic luster, lead gray in color.

A thin splinter of stibnite can be melted easily with a common kitchen match; when melted with a blow pipe on a charcoal block, it produces a heavy odorless white smoke. Stibnite is soluble in hydrochloric acid.

Antimony looks very similar to arsenic and bismuth. It is neither malleable nor ductile but quite brittle and is easily reduced to a powder. Its streak in the streak test is lead gray. When heated in an oxidizing flame with a blow pipe and with no flux, it produces a heavy white volatile sublimate that forms near the assay. This sublimate continues to smoke when the blow pipe is removed.

Arsenic (As)

Specific gravity—4.8. Principal ore: arsenopyrite (FeAsS), also called mispickel, in crystals or massive, of a silvery white to gray-black color.

When an assay of arsenopyrite is melted with a blow pipe on a charcoal block, it gives off a dense white smoke, which at first smells like sulphur or rotten egg, but which then changes and has a strong garlic-like smell. The white fumes given off by antimony are very similar but have no odor.

The heat created by striking arsenopyrite sharply with a hammer will also produce a garlic-like odor. When the assay is heated in a closed test tube, a dark silvery ring of arsenic will form just above the ore, and a mirroring yellow ring will form above it. Under an oxidizing flame, with a blow pipe, arsenic produces a light white sublimate some distance from the assay. The garlic-like odor and the twin rings in the test tube test are fairly positive indications of arsenic, but chemical analysis for quality is necessary.

Beryllium (Be)

Specific gravity—1.847. Principal ore: beryl (beryllium aluminum silicate), pale yellow rhombic crystals in pegmatic dikes.

For testing by ultraviolet light, consult U.S. Bureau of Mines Information Circular No. 7446.

To prepare a wet chemical test, fuse a small amount of your assay with sodium carbonate, powder this fusion, and soak it in a little cold distilled water. From the top of the soaking material, take a few drops with a dropper, being careful not to take any of the sediment (insolubles). Place these few drops in a small clean evaporating dish. In another clean evaporating dish, place five drops of distilled water. This is your blank. In a small beaker, dissolve one sodium hydroxide (lye) pellet in 5 ml of distilled water. To this reagent, add a very small amount of quinalizarin (dye). This will produce a purple-colored solution. Add a drop or two of the reagent to both the blank and the fusion solution. The blank will be violet or purple. The test, if beryllium is present, will be a definite blue.

A blank is often helpful in determining the precise color change caused by the presence of a particular element in a test solution. If in doubt, you can run a known of an element after you get an indicator of it, and compare them for identical appearances.

Bismuth (Bi)

Specific gravity—9.75. Bismuth is obtained chiefly as a by-product in the refining of lead and copper. The principal ore is the mineral bismuthinite (Bi_2S_3). Metallic bismuth is grayish white in color, with a reddish tinge. It is very brittle and tends to be highly crystalline in rhombohedral crystals. Grind up a small portion of your assay and mix it with an equal quantity of potassium iodide crystals and sulphur. Grind this mixture together and heat it with the blow pipe on a charcoal block. A yellow coating with a bright red fringe forms if bismuth is present. Dissolve a small portion of ground ore in nitric acid. When water is added, a white precipitate forms. The streak test for bismuth produces a light gray streak.

Cadmium (Cd)

Specific gravity—8.6. Principal ore: greenockite (CdS) (only commercial ore), a yellow powdery ore found in zinc ores.

Drop a few drops of hydrochloric acid (HCl) on a small amount of powdered assay. A strong odor of rotten eggs will be released; this is not a positive indicator of cadmium, but a good one. Mix a little of the powdered assay with a pinch or two of sodium carbonate, add a drop of water, make a paste, and place it on the charcoal block; then heat steadily in a reducing flame. If the assay contains cadmium, the reducing flame will produce a reddish brown coating near the assay, with an iridescent peacock-blue border.

Calcium (Ca)

Specific gravity—1.55. Calcium is principally found occurring in combination in limestones and calcareous clays.

Dissolve a little of the assay in hydrochloric acid (HCl), add a few drops of sulphuric acid (H_2SO_4), and watch for a white precipitate ($CaSO_4 \cdot 2H_2O$). This will go into solution if you add water and boil. The boiling water test distinguishes calcium from strontium (Sr) and barium (Ba), which will not dissolve in hot water.

Cerium (Ce)

Specific gravity—6.77. Cerium is in the group of trivalent metallic elements called rare-earth metals, or rare earths. There are no simple tests for distinguishing among them, and they can only be identified in a well-equipped laboratory by a good analyst.

Chromium (Cr)

Specific gravity—6.9. Principal ore: chromite ($Fe_3Cr_2O_3$). A bead test of chrome ore will result in a green bead with either a borax bead or phosphate bead. The bead will be green hot or cold and under either an oxidizing or a reducing flame.

Chrome ore, when heated under the blow pipe, will become magnetic. It can also be melted under the blow pipe.

Mix a pinch of the powdered assay with a pinch of potassium nitrate and a pinch of sodium carbonate, dampen with a drop of water, and fuse on a charcoal block with the blow pipe. The fusion is usually yellow if chromium is present.

Fuse a small portion of a mixture of powdered ore and four times its volume of sodium peroxide. Dissolve this, melt in hot water, and filter. If chromium is present, the liquid will be a distinct yellow color.

To test further, make the yellow solution acidic by adding acetic acid drop by drop until litmus paper turns red. When the solution has become acidic, add a few drops of lead acetate solution. If chromium is present, a yellow precipitate will appear. This is lead chromate.

Cobalt (Co)

Specific gravity—8.756. The principal ore is a gray-black quartzite, combined with dark green schist. However, most cobalt is a by-product of refining nickel, silver, and some copper ores.

Using the tip of the blow pipe flame, make a borax bead test. If the bead is blue, the assay is either cobalt or copper. To determine which it is, watch the bead very closely. Just as the blow pipe is removed from the bead, at the moment the red heat disappears, the bead will briefly show green before turning blue as it gets cooler, if the metallic element in the assay is copper alone. If the metallic element is cobalt, however, or cobalt and copper, the bead will be blue hot or cold, and not green at any stage of the test. After a little practice, you can make this test fairly positive.

A little powdered cobalt heated gently in a test tube in dilute nitric acid will turn the acid a rose-red color. Cobalt's color in the streak test is black.

Copper (Cu)

Specific gravity—8.91. Principal ore: chalcopyrite ($CuFeS_2$), also called copper pyrites.

In a test tube, dissolve a pinch of powdered assay in 40 drops of nitric acid. A little heat will help. If the solution is green, it indicates copper. Heat up a clean, bright nail and plunge it into the green acid solution; if copper is present, it will coat the nail with a pink copper plate.

Moisten a small chunk (not powdered) of the assay with a couple of drops of hydrochloric acid; then heat strongly on a small block of charcoal with the blow pipe. A blue or green flame will result if the assay contains copper.

If the candlewick (while the candle is lit) is dipped into some powdered assay, the copper in the assay will give the candle flame a vivid green color. The borax bead test gives three different colors with copper: green when the bead is hot under an oxidizing flame, blue when the bead has cooled after an oxidizing flame, and red when it has cooled after a reducing flame.

Didymium

Didymium is not an element, although at one time it was thought to be one and even had its own symbol (Di). In reality, it is a mixture of oxides of neodymium (Nd) and praseodymium (Pr).

In either the borax or the phosphorus bead test, under either an oxidizing or a reducing flame, and hot or cold, didymium will add a rose color to the bead.

Gold (Au)

Specific gravity—19.32. The natural compounds of gold are tellurides: altaite (a telluride of lead and gold), calaverite (a telluride of gold and silver), sylvanite (a telluride of gold and silver), petzite (a telluride of silver and gold with the silver present in twice the amount of the gold), and hessite (a telluride of gold and silver that is 63% silver).

To test for tellurides in a gold ore, place some ground assay in a test tube and add enough strong sulphuric acid to cover the assay. If the acid turns reddish violet, tellurides are present. Carefully and slowly add water drop by drop until the tellurium precipitates as a gray-black sediment.

To test for gold, dissolve the powdered assay in aqua regia (one part nitric acid to three parts hydrochloric acid) in a test tube, boil the solution gently for 4 or 5 min, and then let it cool. In another test tube, dissolve a few crystals of stannous chloride ($SnCl_2$) in 20 drops of hydrochloric acid (heat gently).

Place a drop of the acid solution from the assay onto a paper napkin or filter paper. Add a drop of the stannous chloride solution to the assay drop (this is called a spot test). A pale pink to dark purple color will appear if gold is present. The darker the color, the richer the assay. This is a positive test. Mix the stannous chloride solution fresh: Its shelf life is very limited.

You can dissolve a small piece of gold in some aqua regia, double its volume with water, and keep this in a well-corked bottle as a check to ascertain if your stannous chloride solution is still active.

The following test for gold is also positive. Dissolve everything in the powdered assay that will go into solution in aqua regia. Add water to double the volume, and filter out the residue that is left behind. Boil the aqua regia solution until it is syrupy (this expels the nitric acid) and then double its volume with water. To this solution add ferrous sulphate solution—you can make this by dissolving a pinch or two of ferrous sulphate ($FeSO_4$) in hot water and adding a few drops of hydrochloric acid to produce a clear green solution. When the ferrous sulphate solution is added to the assay solution, any gold present precipitates as a fine brown powder (pure gold), which can be easily melted into a gold bead under the blow pipe.

Tellurium is the only element that combines chemically with gold.

Iridium (Ir)

Specific gravity—22.65. Iridium is in the platinum group of elements. It is insoluble in all acids, including aqua regia, and cannot be melted under the blow pipe—its melting temperature being 2,443°C. It is found in the nickel–copper ores of Canada.

Particles that you suspect of being iridium should be placed in a small evaporating dish with a pinch or two of sodium nitrate (saltpeter), and fused over a spirit lamp. To the fusion add aqua regia (one part nitric acid to three parts hydrochloric acid); a deep red or red-black solution indicates iridium.

Iron (Fe)

Specific gravity—7.65. Principal ores: magnetite (Fe_3O_4), hematite (Fe_2O_3), magnetic pyrites, and carbonates of iron.

Check your assay with a magnet; if it is not magnetic, heat it with a reducing flame under the blow pipe, and recheck with the magnet. If the assay contains iron, the magnet should now pick it up.

Boil a finely crushed sample of the assay in a test tube in dilute nitric acid solution (one part acid to one part water) for 4 or 5 min. When the solution has cooled, add water to increase the volume of liquid by about one-quarter. To this, add strong ammonia (NH_4OH), drop by drop, until the iron, if any, precipitates as a red or brown mass.

A very sensitive test is done by boiling the powdered assay in hydrochloric acid for a couple of minutes and, when it has cooled, adding two or three drops of nitric acid and a little additional water to the solution. A drop of sulphocyanate added to this solution will produce a deep red color if iron is present.

See also the borax bead test for iron oxides on page xxx.

Lead (Pb)

Specific gravity—11.34. Principal ore: galena.

Mix some powdered assay with a charcoal flux (one part borax, one part sodium carbonate, one-half part powdered charcoal). Make a paste of the mixture with a little water and place this on a charcoal block. Fuse it with a reducing flame (which will appear blue) under the blow pipe. A yellow coating will be evident near the assay and a lead bead with white border will lie in the center of the block.

Boil some ground assay in a solution, three parts water to one part nitric acid, for 1½–2 min; then filter it through a filter paper or paper napkin. To the cold filtrate, add a few drops of dilute hydrochloric acid (three parts water to one part acid). If a white precipitate is thrown down, this is a chloride of mercury, silver, or lead. Heat the solution. If the precipitate disappears (dissolves) and is thrown down again when the solution is cold, it is lead. Silver and mercury will not dissolve on heating.

Manganese (Mn)

Specific gravity—7.42. Principal ore: manganese dioxide (MnO_2). Manganese is widely dispersed, occurring in many ores.

Heat a sodium carbonate bead with just a speck of assay in an oxidizing flame; when cooled, the bead should look bluish green. Boil some powdered assay in hydrochloric acid; it will produce a black to greenish black solution if manganese is present in the assay. See also borax bead test for iron oxides on page xxx.

Mercury (Hg)

Specific gravity—13.596. Principal ore: cinnabar (HgS). Any rock that shows red powder when ground should be checked for mercury.

Rub some of the powdered assay on a clean copper coin; if the coin is silvered, the assay contains metallic mercury. Under the blow pipe, the powdered assay will volatilize and go off as a fume. Remember that mercury is poisonous in many of its forms.

If an assay containing mercury is heated in a long test tube, globules of mercury and sulphur form. See the closed tube test for mercury on page xxx.

Molybdenum (Mo)

Specific gravity—10.2. Principal ore: molybdenite (MoS_2). A metaphosphate bead, when cooled after having been touched to a molybdenum assay and heated in a reducing flame, appears pale green in color.

Heat a thin fragment of molybdenite with an oxidizing flame under the blow pipe. The flame will be colored a yellow-green.

When a powdered assay containing molybdenum is heated on a charcoal block in an oxidizing flame, the area close to the assay becomes copper red with a white border.

Nickel (Ni)

Specific gravity—8.84. Principal ore: pyrrhotite (magnetic pyrites). Nickel also occurs in other sulphides, and in arsenides.

Boil a pinch of powdered assay in dilute nitric acid (one part nitric acid to two parts water). Remove any iron that is present by adding strong ammonia (NH_4OH), drop by drop, until the iron precipitates, and then filtering. To the filtrate, add dimethylglyoxime solution, drop by drop, until a rose-colored precipitate appears. This is a nickel compound.

To make dimethylglyoxime solution, dissolve a pinch of dimethylglyoxime (a yellow powder) in ½ ounce of acetone, pure grain alcohol, or vodka.

A borax bead, touched with nickel and heated in an oxidizing flame with the blow pipe, will be violet when hot, red-brown when cold.

Niobium (Nb) [Columbium (Cb)]

Specific gravity—8.57. Niobium was formerly named columbium, and it is still generally known by that name in the metallurgy trade. It occurs in the minerals columbite ($FeNb_2O_6$) and tantalite ($FeTa_2O_6$), from which it is separated only with considerable difficulty. It closely resembles tantalum (a noble metal). The two metals niobium and tantalum always are found together, never alone. There is no easy test for distinguishing them. This must be done in a well-equipped laboratory.

Fuse several beads composed of the assay plus five volumes of borax on a platinum double loop. Crush these and boil the powder in hydrochloric acid to a clear solution. Add a small piece of pure zinc (Zn) metal and boil. If niobium is present, the solution becomes blue; with continue boiling, it becomes brown. If the solution is diluted with H_2O, it becomes colorless.

Osmium (Os)

Specific gravity—22.5. Osmium is a platinum-group metal and is not affected by common acids or aqua regia. The tetroxide form of osmium is highly poisonous. The identification of anything suspected of being osmium or of containing osmium should be performed in a well-equipped laboratory by a chemist.

When osmium is heated in an oxidizing flame under the blow pipe on a charcoal block, the resulting odor is extremely disagreeable and the fumes cause the eyes to smart.

Palladium (Pd)

Specific gravity—12.10. Palladium is another member of the platinum family of metals. Dissolve the assay suspected of containing palladium in aqua regia (one part nitric acid to three parts hydrochloric acid), boil until the solution is syrupy, and add an equal volume of water. Then filter the solution.

Place a drop or two of the filtered solution in a clean test tube, add a drop or two of stannous chloride solution [a small amount of crystalline stannous chloride ($SnCl_2$) dissolved in 20 drops of gently heated hydrochloric acid]. You will first see a deep yellow color, which after a few minutes will turn blue-green if palladium is present.

Another positive test is to dissolve a pennyweight of dimethylglyoxime in 5 ounces of hot water, filter, and let cool (this solution keeps well). Add this solution to your assay solution (from above), drop by drop. If palladium is present, a voluminous yellow precipitate of palladium dimethylglyoxime will appear.

Platinum (Pt)

Specific gravity—21.45. Platinum occurs native (that is, in its pure elemental state) in small flat grains or pebbles in alluvial sands. The only platinum ores are sperrylite ($PtAs_2$) and cooperite, both very rare.

Dissolve an assay suspected of being platinum in hot aqua regia (one part nitric acid to three parts hydrochloric acid). Boil this solution down to the consistency of syrup, and then add water to double the volume. Next, dissolve a tablespoon of good quality ammonium chloride (NH_4Cl) in a little water. Add the ammonium chloride solution slowly to your assay solution until a bright orange precipitate appears. If platinum is present in the assay, this orange precipitate is ammonium chloroplatinate.

Rhodium (Rh)

Specific gravity—12.44. Rhodium is another of the rare metals of the platinum family.

Fuse a few of the particles that you suspect of being rhodium together with a pinch of potassium bisulphate ($KHSO_4$) under the blow pipe. Boil the fusion in aqua regia (one part nitric acid to three parts hydrochloric acid) for a minimum of 5 min. Filter and then add a few drops of pure grain alcohol to the filtrate. If rhodium is present, a black precipitate will appear.

Ruthenium (Ru)

Specific gravity—12.2. Ruthenium is another platinum-group metal; it is obtained from the residue of platinum ores by heat reduction.

Mix a pinch of both potassium hydroxide (KOH) and potassium chlorate ($KClO_3$) with a few grains of the assay and fuse them under the blow pipe in a strong flame. When the fusion has cooled, add it to hydrochloric acid, boil for a minimum of 5 min, and filter. The filtrate, if orange colored, indicates ruthenium. A little nitric acid added to the filtrate will produce a black precipitate.

Accurate and positive identification of platinum and its sister metals can only be carried out in a well-equipped laboratory by a skilled chemist.

Selenium (Se)

Specific gravity—4.79. Selenium is primarily produced as a by-product of copper refining. However, the black shale of Idaho contains up to 1 pound of selenium per ton.

Heat your powdered assay under the blow pipe on a charcoal block. If the assay contains selenium, it will smell like rotten radishes—a musty, decaying odor—and give off a dirty brown smoke. A silver coating will also appear on the charcoal block, some distance from the assay, with a brown or red collar.

The silver-colored deposit on the charcoal block, if heated with a reducing flame under the blow pipe, will become an azure blue color.

Silver (Ag)

Specific gravity—10.7. Silver does occur in the native state as pure silver, but more commonly it occurs as silver sulphide (Ag_2S) or silver chloride (AgCl).

Silver chloride is called horn silver. It constitutes the upper zone of silver veins and is theoretically 75.3% silver. Silver chloride is a pearl gray color; it is massive and resembles wax.

Mix a pinch of the powdered assay with three times its volume of sodium carbonate (Na_2CO_3) (baking soda), and place the mixture on a charcoal block. Fuse the mixture, using the blow pipe, until a bright globule of silver is formed. It will remain bright even after cooling.

Place a pinch of the powdered assay in a test tube containing nitric acid and boil. Filter the solution and add a pinch of table salt. A white, curdy precipitate of silver chloride (AgCl) will appear. Place some of this precipitate in the sunlight, and shortly it will turn purple. Silver chloride is very soluble in ammonia. When heated strongly under the blow pipe, it converts into metallic silver.

Strontium (Sr)

Specific gravity—2.5. Principal ore: celestite ($SrSO_4$). Strontianite ($SrCO_3$) is a less common strontium-bearing mineral. Celestite closely resembles barium but is not as white, is slightly harder, and is less reactive.

When a crushed sample of the assay is heated strongly under the blow pipe, a brilliant red color appears in the flame; a drop or two of hydrochloric acid on the assay will intensify this brilliant red.

Do not confuse strontium's flame color with that of calcium, which is a yellowish red. Strontium is used to produce red flares. This is the color which you are looking for.

Tantalum (Ta)

Specific gravity—16.6. See the comments about this element under niobium (Nb) [columbium (Cb)].

Tin (Sn)

Specific gravity—7. Principal ore: cassiterite (SnO_2). Stannite (Cu_2FeSnS_4) is a less common tin ore. Tin is never found in its metallic state in nature. Cassiterite is usually brown to black but can also be white or red. Tin's color in the streak test is white to off-white.

Mix some powdered assay with three times its volume of baking soda. Moisten the mixture, and heat it strongly on the charcoal block under the blow pipe; a small globule of tin will form.

Another test is to boil a pinch of assay mixed with a pinch of zinc powder in a little dilute hydrochloric acid (one part acid to three parts water). Bright, silvery tin will form.

Titanium (Ti)

Specific gravity—4.2. Principal ore: rutile (TiO_2). Rutile can be red, red-brown, yellowish, or black. The streak test color for titanium is light brown. It cannot be melted under the blow pipe.

Make up several beads of ore part powdered assay and five parts sodium carbonate with the blow pipe and a platinum wire loop. Crush these beads up and add to them 1 teaspoon of dilute sulphuric acid (one part acid to three parts water). When this mixture stops bubbling, add 5 teaspoons of water. A few drops of peroxide added to this will, if titanium is present in the solution, turn the solution yellow or brownish yellow.

Tungsten (W)

Specific gravity—17. Principal ores: scheelite ($CaWO_4$) and wolframite [$(Fe,Mn)WO_4$]. Tungsten is obtained as a powder by reduction of the oxide.

Place a good-sized pinch of crushed assay in a test tube containing a teaspoon of hydrochloric acid. Boil until a canary yellow residue is formed, then add a small piece of zinc to the yellow solution. The solution will turn deep blue and then brown if tungsten is present. The yellow residue in such a case is tungstic acid (H_2WO_4) and is soluble in ammonia.

Tungsten can be panned out of the crushed assay, just as gold is panned, because of its specific gravity. It will not fuse under the blow pipe.

Uranium (U)

Specific gravity—18.3. Uranium is not found in a native (pure) state. Uranium is principally produced as a by-product of the extraction of radium (Ra); it is chiefly found as an oxide in the minerals pitchblende and carnotite.

There is no simple, foolproof field test for uranium. Carnotite is radioactive and melts easily under the blow pipe. Pitchblende is pitch-black with an olive green streak and cannot be melted under the blow pipe. A borax bead made on a platinum wire with a few specks of pitchblende added is yellow in an oxidizing flame and pale green in a reducing flame.

Vanadium (V)

Specific gravity—6.02. Principal ores: carnotite, patronite, roscoelite, and vanadinite.

A borax bead with a few specks of powdered assay will become a fine green when cooled after heating in a reducing flame; it will become a very light yellow if heated with an oxidizing flame. The most positive test is to fuse a finely ground assay with sodium carbonate (Na_2CO_3). Boil the fusion in water, filter the solution, and add an excess of hydrochloric acid to the filtrate; when the filtrate has cooled, add hydrogen peroxide (H_2O_2). If vanadium is present, the solution will turn a brilliant red color.

Zinc (Zn)

Specific gravity—7.13. Principal ore: sphalerite (ZnS), or zinc blende.

Mix some powdered assay with a couple of pinches of charcoal flux (two parts sodium carbonate, two parts borax, one part charcoal). Make a paste of the above mixture with a little water, place it on a charcoal block, and fuse it with a reducing flame under the blow pipe. There will be a white coating near the assay with a narrow blue border.

Place a drop of cobalt nitrate solution (a pinch of cobalt nitrate crystals dissolved in ½ ounce of water) on the white coating around the assay, and then reheat the assay with a reducing flame under the blow pipe. When it has cooled, the coating will be a bluish green if the assay is zinc-bearing.

Test Results

Some tests are conclusive, and some are inconclusive but provide clues that should be followed up by additional tests for a better confirmation.

You will, at times, want to determine the metallic ions contained by a particular solution. There are many ways this can be done: by cementation, by evaporation, by electroplating, and by using various reagents to precipitate something recognizable out of the solution. In some cases, the assay is put into a solution to test; and in some cases, it is put into solution and combined there with a reagent to produce a precipitate that is subjected to another test. Some tests only give an indication in acidic solutions; others only work in basic solutions.

The common type of precipitation (precipitate formation) used in chemical analyses and extractive procedures occurs by double decomposition when two solutions are mixed. If each of the solutions contains one radical of an insoluble compound, the precipitate they form will appear as an insoluble (solid) in a solution. For example, if silver is dissolved in nitric acid, the solution is silver nitrate; if this solution is evaporated to crystals, the crystals are silver nitrate ($AgNO_3$). If instead you added a chloride to the solution of silver nitrate, the silver would be precipitated out as silver chloride (AgCl), a white powder. The powder is the precipitate, which is no longer soluble in the solution.

If you were to hang a strip of copper in the silver nitrate solution, copper ions would go into the solution and silver crystals would form on the copper. This process is known as cementation. Copper ions have replaced the silver ions in the solution.

Suppose you had a metal you thought was nickel and had dissolved it in nitric acid, noting the color of the solution and so forth. If you next added DMG to the solution, no reaction would take place; however, if you neutralized the solution with ammonium hydroxide (ammonia water), added some additional ammonium hydroxide to make the solution definitely basic, and then added a drop or so of the DMG reagent, a scarlet precipitate would appear if the metal was indeed nickel. Boiling and then cooling the solution, with the precipitate still in it, will cause beautiful red needles to form, a positive test for nickel.

Often, a salt is the substance in question. Under the blow pipe, some salts will reduce to the metal that was in them. However, some metallic salts are destroyed by heat. In such a case, you would want to put the salt into solution and then test with a reagent for a recognizable precipitate, or with an introduced metal strip for cementation. Great caution must be exercised in testing so as not to produce a toxic gas or explosive compound or reaction.

Suppose you have some yellow to red crystals and some colorless white crystals. When you dissolve some of the yellow-red crystals in an inch or two of water in a test tube and make the solution acidic by adding hydrochloric acid (HCl) and then spot test this solution with stannous chloride ($SnCl_2$), the test gives a positive reading that the red-yellow crystals are a gold salt, probably gold trichloride ($AuCl_3$).

Now, if you treat the colorless crystals in the same manner, you could come up with lots of bubbles that are gaseous hydrocyanic acid (HCN), which is deadly if breathed. The colorless crystals in this case could also be a gold salt—gold cyanide [$Au(CN)_3 \cdot 3H_2O$]. The lesson you should learn from this is: Work under the hood, with draft, especially when you are testing an unknown.

Be extremely careful with all chemicals and reactions, especially with cyanides, cyanide solutions, and metallic cyanide salts.

Junk Yard Tests

Anyone purchasing ferrous or nonferrous scrap metal must make a simple and quick evaluation and identification of exactly what is being offered; that is, is it steel? If so, what kind or grade, and so forth. This knowledge of rapid identification with a high degree of accuracy should be known by the buyer and the seller. If not, one is at the mercy of the other.

Many factors are involved. If the origin of the scrap is known and it is all the same material, this narrows it down considerably. For example, if you have all Ford auto radiators, cores, and tanks briquetted, you know that when it is all melted down you will wind up with ingots that will analyze close to 80.75% copper, 3.25% tin, 5.50% lead, and the balance zinc. If you have a load of mixed briquetted radiators (Ford, GM, Chrysler, etc.) melted together, you wind up with close to 60% copper, 5.0% tin, 12% lead, and the remainder zinc. As you see, you have quite a spread between the two, which makes for a big difference in selling price or buying price. Of course, if you have aluminum auto pistons, you pretty much know that all pistons fall into a narrow range of aluminum–silicon alloys. In this case, the only thing that concerns you is, Are they clean and free from rings (cast iron), wrist pins (steel), and wrist pin retainers (steel). This changes the price.

The most basic tests are visual, heft, spark, and magnetic. What does it look like, is it heavy, mediumweight, or lightweight? Does it throw sparks when held against a grinding wheel? Let us look at the metals that are most common.

Weight and Color

Aluminum: SG 2.7; color—tin white
Antimony: SG 6.62; color—silver white
Arsenic: SG 5.7; color—steel gray
Barium: SG 3.66; color—yellowish white
Beryllium: SG 1.8; color—steel gray
Bismuth: SG 9.8; color—white with reddish tinge
Cadmium: SG 8.64; color—white with blue tinge
Calcium: SG 1.54; color—yellowish white
Cerium: SG 6.7; color—steel gray
Cesium: SG 1.8; color—silver white
Chromium: SG 7.19; color—grayish white
Cobalt: SG 8.8; color—silver white with bluish tinge
Columbium: SG 8.57—color steel gray
Copper: SG 9; color—reddish orange
Gallium: SG 5.9; color—silver white
Germanium: SG 5.3; color—grayish white
Gold: SG 19.32; color—yellow
Indium: SG 7.3; color—silver white
Iridium: SG 22.65; color—gray
Iron: SG 7.9; color—grayish white
Lead: SG 11.34; color—blue gray
Lithium: SG 0.53; color—silver white
Magnesium: SG 1.75; color—silver white
Manganese: SG 7.44; color—white gray

Mercury: SG 13.55; color—white
Molybednum: SG 10.3; color—dull silver
Nickel: SG 8.88; color—white
Osmium: SG 22.5; color—blue white
Palladium: SG 12.00; color—white
Platinum: SG 21.45; color—grayish white
Potassium: SG 0.86; color—silver white
Radium: SG 5.00; color—brilliant white
Rhodium: SG 12.4; color—bluish white
Rubidium: 1.525; color—white
Ruthenium: SG 12.3; color—white
Selenium: SG 4.81; color—steel gray
Silver: SG 10.5; color—white
Sodium: SG 0.97; color—white
Strontium: SG 2.6; color—yellowish white
Tantalum: SG 16.65; color—iron gray
Tellurium: SG 6.24; color—shining white
Thallium: SG 11.85; color—white
Thorium: SG 11.5; color—grayish white
Tin: SG 7.29; color—bright white
Titanium: SG 4.5; color—dark gray
Tungsten: SG 19.3; color—
Uranium: SG 19.07; color—bright silver
Vanadium: SG 6.11; color—brilliant white
Zinc: SG 7.1; color—bluish white
Zirconium: SG 6.53; color—silvery white

The specific gravity (SG) given here is the relative density of a substance to the density of pure water, which is SG 1. The SG is given for the metals in their pure state, as is the color.

Those Metals which are Magnetic

Nickel: slightly magnetic
Platinum: para magnetic
Tungsten carbide: magnetic
Stellite: magnetic

Stainless steel: magnetic

High-speed steel: magnetic

Carbon steel: magnetic

Magnitite black sands: magnetic

Most ferrous metal oxides: magnetic

Most ferrous alloys (that is, cast iron and an alloy of iron and carbon): magnetic

Metals which Can be Identified by the Spark Test

Nickel: 10-in. light orange spark

Tungsten: 2-in. very light orange spark

Stellite: 10-in. light orange spark

Stainless steel: heavy 40-in. white spark, forked

Cast iron: red sparks very short

Mild steel: heavy 50-in. white to straw yellow, forked

Pure iron: bushy, very bright sparks like a "Fourth of July sparkle"

Practice with known material against the wheel, and in no time you will be able to quickly identify unknown material. See Figure 3.51.

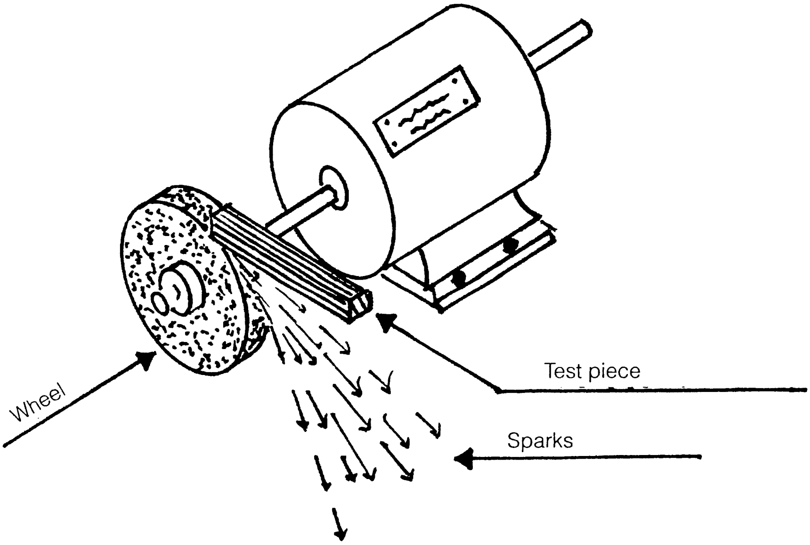


Figure 3.51. Application of material being tested to abrasive wheel to produce sparks

Non-Destructive Testing with Reagents

I have covered a good number of tests where you use the blow pipe and various reagents to put the sample into solution and then identify it by its reaction when another reagent is added to the solution containing the metallic ions. Identification is then by color, precipitant produced, and so forth. Nondestructive testing with liquid reagents is the method of applying a drop of reagent to a small area of the metal in question which has been cleaned of any surface grease, paint, patina, and so forth, with steel wool or a file. The spot being tested must be down to a clean metallic surface.

The test is nondestructive overall, except you might have a small amount of etching and or discoloring. See Figure 3.52.

The following reagents are required for nondestructive junk yard identifying tests:

1. Full-strength nitric acid.
2. Full-strength hydrochloric acid.
3. Saturated silver nitrate solution.
4. Potassium ferrocyanide saturated solution.
5. Dimethylclyoxime 1 gram dissolved in 50 ml of glacial acetic acid, concentrated ammonium hydroxide solution (30 ml) diluted with one-third distilled H_2O. When everything is in solution, add 10 g of ammonium acetate.

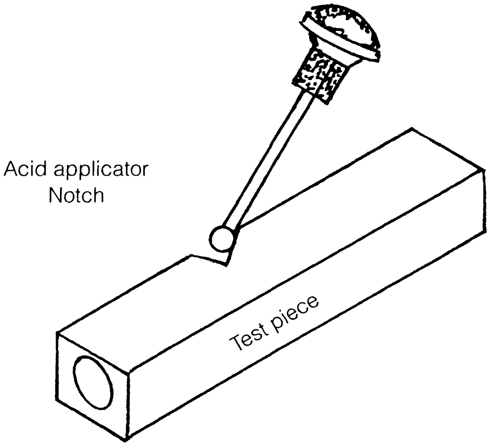


Figure 3.52. Application of reagent drop to clean surface of metal being tested to produce a reaction

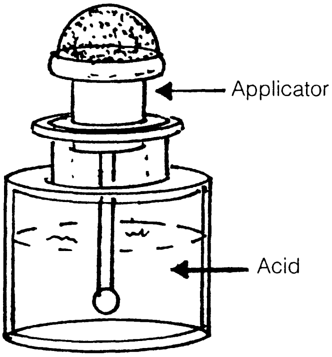


Figure 3.53. Glass spotting bottle containing test reagent

The five reagents are each placed in its own touch bottle and labeled 1 through 5, including the contents. See Figure 3.53.

Reagent #3 (silver nitrate—$AgNO_3$) is made by dissolving pure silver in nitric acid HNO_3. $Ag + HNO_3 \rightarrow AgNO_3$. Now, if any chloride-containing salts or liquids are added to $AgNO_3$, the silver will precipitate out as AgCl (silver chloride), a white curdy mass. Therefore, when making it up, make certain that any water or HNO_3 is free of any chlorine (that is, HCl, NaCl, etc.). If you wash the testing glass policeman under the faucet and return it to your $AgNO_3$ test solution, you can contaminate it by precipitating the $AgNO_3$ as AgCl.

Reagent #4 [Potassium ferrocyanide, $K_4Fe\ (CN)_6$] has a low toxicity. However, if heated to a red heat it evolves highly toxic fumes.

Reagents #1 and #2 (HNO_3 and HCl) mixed together form aqua regia in the proportions of one part HNO_3 to three parts HCl give you aqua regia, a solvent for gold. It is only good practice to avoid cross-contamination of your reagents.

Performing Junk Yard Tests

Using our five reagents, clean a small surface on the metal in question, free from grease, corrosion, rust, paint, and, with steel wool, sand paper, or a file. Take a guess as to what you have, choose one of your reagents, and apply one drop to the clean metallic surface and observe the color change and reaction, if any, caused by the reagent. See Figure 3.54.

Test for gold: Although gold scrap (that is, old jewelry, etc.) can be tested by applying a drop of reagent #1 (HNO_3), you will get a clear no-action response from 24 kt (pure) to 14 kt, and from 14 kt downward. The spot will show a brown discoloration getting browner and browner as you move down in purity. Where this test is valid is when checking to see if the object is solid gold, gold plated, or rolled gold (old term: gold filled). In both cases, you must notch the

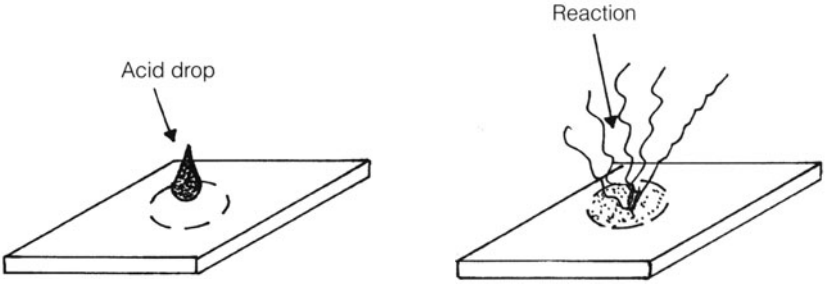


Figure 3.54. Observing color of fume reaction produced by reagent applied to material being tested for identification

object with a three-cornered file deep enough to get through the gold plate or rolled gold down to the base metal (usually brass). See Figure 3.55.

A drop of reagent #1, HNO_3, applied to the notch will bubble and turn green with red smoke. Rolled gold can fool you if you do not cut the notch deep enough, as in some old high-grade rolled-gold jewelry, the gold was quite thick.

Rolled (gold filled) is produced by sweating or soldering carat gold sheets on to a base metal core—usually an alloy of 90% copper and 10% zinc. This sandwich is then rolled into a sheet, tube, or wire. If the inner core is sterling silver, the object is usually marked with a silver hallmark. See Figure 3.56.

To be sure of the results when testing gold, use both the notch and reagent #1 and test needles. See Figure 4.16.

Test for silver: Placing a drop of reagent #1 (HNO_3) on a clean area should show no color. Now, add one drop of distilled eater on top of reagent drop, and then add one drop of reagent #2 (HCl). If the metal is silver, you will get a white curdy precipitation. If the curdy precipitant has some discoloration of green or

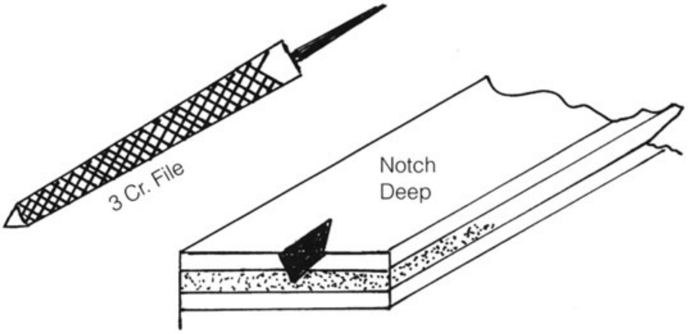


Figure 3.55. Notched gold-filled material for acid test

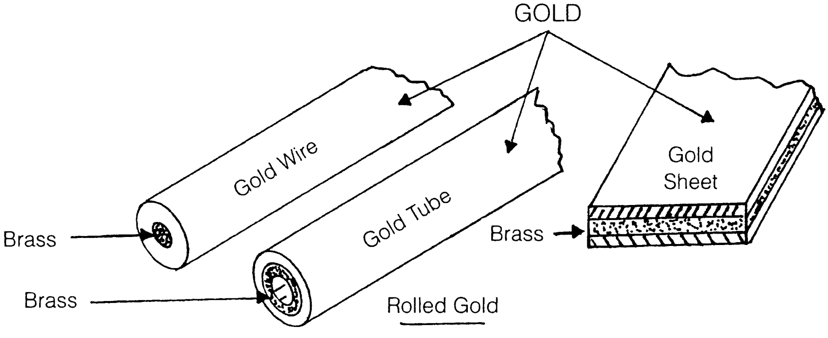


Figure 3.56. Cross section of gold-filled (gold-rolled) material

greenish blue mixed in with the white (silver chloride), the metal is sterling silver. Sterling silver is 92.5% silver and 7.5% copper.

Test for nickel silver: One drop of reagent #1 (HNO_3); color—green with brown smoke.

Test for brass: One drop of reagent #1 (HNO_3); color—light green.

Test for cupronickel: One drop of reagent #1; color—green. Add one drop each of reagents #2 and #5; color changes to red.

Test for nickel silver: One drop of reagent #1; green color and brown smoke.

Test for brass: One drop of reagent #1 (HNO_3); color—light green.

Test for manganese bronze: One drop of reagent #3 ($AgNO_3$); test spot turns black.

Test for nickel: One drop of reagent #1; color—pale green.

Test for aluminum: One drop of reagent #3 ($AgNO_3$); no color change.

Test for magnesium: One drop of reagent #3 ($AgNO_3$); no color change.

Test for zinc: One drop of reagent #1 (HNO_3); effervescence with brown smoke.

Test for tin: One drop of reagent #1 (HNO_3); surface turns yellow, giving off yellow smoke.

Test for tin via ear: Tin has a peculiar characteristic no other metal seems to have. If you hold a piece of pure tin up to your ear and bend it, you will hear a strange musical noise, tingling somewhat like tiny bells. If it sings to you, it is tin for sure.

Test for platinum: No reaction to acids.

Test for palladium: One drop of reagent #1 (HNO_3); a brown discoloration.

Analysis of a Metal Surface via Electrographic Technique

In the case where the object to be analyzed is of archeological importance (a rare coin or any metal object which you would dare not etch or affect the surface in any manner that would deplete its value as an artifact), one must resort to a simple electrographic technique. This system is used quite often by coin collectors and dealers. As only a very few milligrams of the surface is removed, the speciman remains almost completely unaffected.

To analyzing a rare coin via the electrographic technique, the following procedure must be followed:

Step 1. Clean both sides of the coin by rubbing with a paste of baking soda and water and rinse under hot water; this makes the face a good electrical conductor.

Step 2. Moisten a circle of white filter paper (which is large enough to extend ½ in. beyond the coin when layed in the center) with a saturated solution of potassium nitrate.

Step 3. Place the filter paper which is dampened with potassium nitrate on a clean, dry glass surface.

Step 4. Place the coin in question in the center of the filter paper.

Step 5. Using a 1.5-V dry cell or DC power source, connect two platinum wires, one to the positive side and one to the negative side of your power source (1.5 V DC)

Step 6. Touch the positive Pt wire to the coin. This makes the coin the anode (+). The negative Pt wire is touched to the damp filter paper, making the filter the cathode. The connection is made for only a few seconds. What happens is an anodic disolution of the metal constituents of the coin which is transported to the filter paper dampened with potassium nitrate. Now rotate the coin to a new position. Again, apply the voltage the same length of time. Do this once again as above.

Step 7. Digest the filter paper in nitric acid. You now have the various constituents of the coin in solution as nitrates. Continue the procedure via wet chemical or the analytical method of your choice.

4

Recovering and Refining Values from Secondary Sources

Secondary sources comprise such things as scrap jewelry, electronic scrap, old coins, and spent plating solutions.

First, I will explain the terms electrowinning, extraction, parting, and refining. Electrowinning is a term much used in conjunction with parting and extraction. It is a very uncomplicated electroplating system that consists of putting metallic ions in an acidic or basic solution (called the electrolyte) from an anode that is an impure alloy of the desired metal and other base metals, and plating the desired ions as metallics onto a pure cathode or an inert (insoluble) cathode. It is not really a winning process but a refining (purifying) process: You have not won anything because you already had it as an anode or as ions in solution.

The terms extraction and parting are used as follows: If you have an alloy of yellow gold (gold and copper) and you separate the two of them, you can say either that you have extracted the gold from the copper or that you have extracted the copper from the gold; in either case, you have parted the two. If you wished to obtain pure copper and pure gold from your parting operation, you would have to refine each. The degree of refining in each case would be based on the intended end use of each. The parting alone might leave either the gold or the copper at sufficiently purity for its intended use; if not, you might refine further or re-refine.

Imagine, for example, that you have some mercury that is carrying some gold or silver. Place the mercury in a retort and heat it to the vaporizing temperature of the mercury; these vapors will leave the retort and travel through a water-cooled condenser, which will cool them below vaporizing temperature so that they recondense into liquid mercury. The liquid mercury can then be caught in a receiver. As the gold or silver was never anywhere near its vaporizing temperature, most of it stayed behind as a solid in the retort. However, some of the gold or silver did get carried across, in the form of solid particles, by the mercury vapors. The mercury is thus purer than when you started, but it can be further purified by cleaning out the retort and running the mercury through again and again. If you simply wished to use the mercury to collect fine gold or silver in a sluice or gold pan, or to fill stamp mill mercury wells, the first pass would be sufficient. If, however, you needed chemically pure mercury for use as a special reagent, you would have to resort to redistilling (re-refining, repurifying).

It is common practice to refine by one method and re-refine by another. This goes for all extraction and refining processes. An error made by many small operators is to carry the final material to too high a fineness—to the point of diminishing returns. You never can come up with an absolutely pure product.

The working examples that follow are simply a series of partings, selective separations, and precipitations. It is never wise to work with too large a batch of material at a time. Even commercial precious metal companies work in a series or with multiple batches. It is much safer and simpler to reduce 5 lb. of scrap in five or more separate batches singly, or in five separate units at once, than all in a single batch.

While learning, work with very small batches; then, increase the size of your operations as you become skilled at them.

Recovering Silver

The first working example is the recovery of silver from 20 pennyweights of clean sterling silver scrap. As with anything, you must have a plan. See Figure 4.1. Figure 4.1 indicates the physical chemical steps involved. Clean scrap means

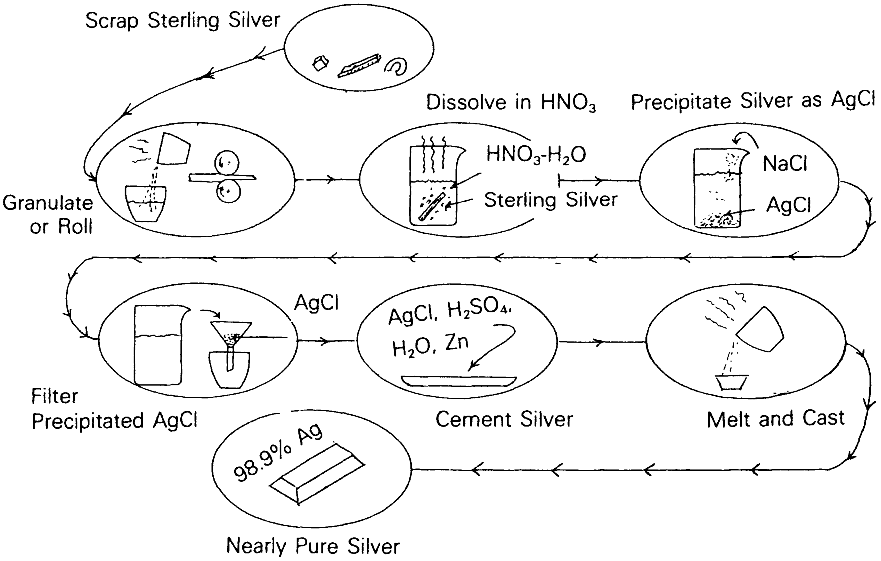


Figure 4.1. Simple recovery of silver from sterling silver

scrap that is free from any organic materials, gangue, or other metallic alloys. Clean sterling silver is composed entirely of silver and copper.

Step 1. In order to hasten the digestion of the sterling silver by the nitric acid, you must have maximum surface area for the acid to work on. Unless the material is already finely divided or quite thin, you will have to reshape it. There are two choices: to granulate the material or to roll it out thin.

To granulate, melt the silver in a hand crucible with an oxygen natural gas torch and pour it (in a thin stream) into a 5-gal container that is three-quarters full of cold water from a height of 3 or 4 ft, moving the crucible in a circular motion. Placing 1 in. of clean white silica sand on the bottom of the container ahead of time prevents any pellets or granules from welding themselves to the bottom of the container and also allows you to use a plastic container. See Figure 4.2.

To roll, heat the material to a dull red and chill it in cold water to anneal it. Then roll it very thin in a jeweler's roll. The thin material is twisted into what are called cornets to prevent them from lying flat in the digesting flask. See Figure 4.3.

Step 2. Place the granulated or rolled silver cornets in an Erlenmeyer flask equipped with a spin bar and place it on a hot plate. Start the bar spinning slowly, and cover the silver with a 1-to-1 solution of nitric acid (HNO_3) and distilled water (H_2O); the material should be covered by at least a ½ in. of this solution. Set the heat on low and watch for the acid to start acting on the silver. The

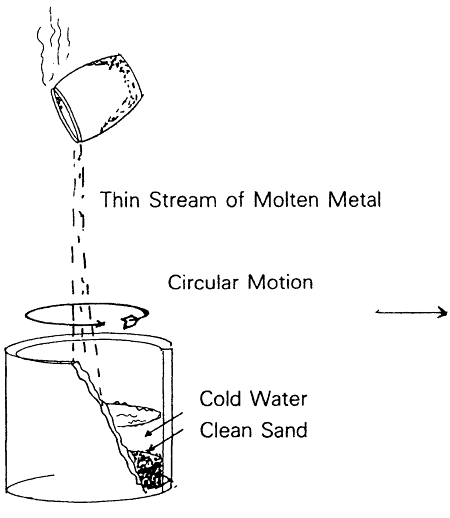


Figure 4.2. Granulation

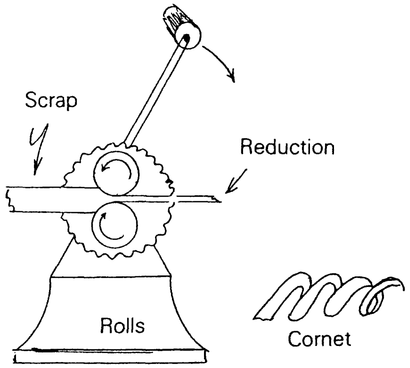


Figure 4.3. Rolling scrap to make it thin; example of a cornet

solution will begin to react, giving off reddish brown fumes. These fumes are mostly oxides of nitrogen, products of the interaction of nitric acid with base metals (in our case, the copper in the sterling silver). You will see these fumes over and over again in the reactions of nitric acid with other substances: They are toxic, suffocating, and extremely corrosive, so work under a forced-draft hood.

When the reaction starts, the heat may be turned off because the reaction itself is exothermic (produces heat). Note the change of color of the solution due to the copper in the sterling—a dark blue-green. See Figure 4.4.

When the action ceases (the acid is spent), check to see if all the metal is in solution. If there is some undissolved silver material, decant most of the solution into a large beaker, being careful not to carry over any sediment. Then add fresh 1-to-1 nitric acid and distilled water, a little at a time, until everything is in solution. Dilute this solution with three volumes of distilled water and filter it into the solution you decanted off from the first digestion. Examine the residue, if there is any, on the filter, and set it aside to dry.

The exact amount of nitric acid solution needed to digest a material will vary. To avoid wasting acid, work with small additions of acid until all the material is digested. After everything is digested, some operators add small amounts of silver to use up the unspent acid; when a little more silver is added and is not dissolved, it indicates an end point (the acid is spent). This undissolved addition is filtered out of the solution and is used in the next batch. See Figure 4.5.

This operation can be performed in a Pyrex bowl or pie dish, or on a sand bed in a steel gold pan, on the gas hot plate. See Figure 4.6.

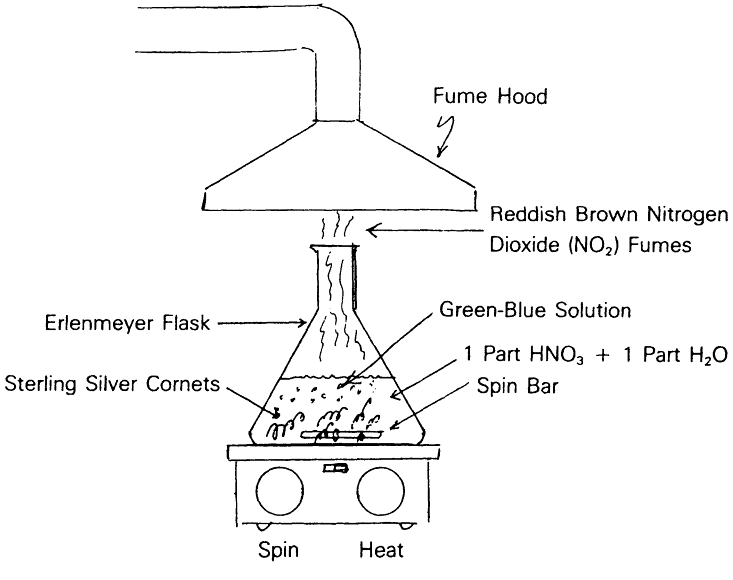


Figure 4.4. Digesting sterling silver scrap

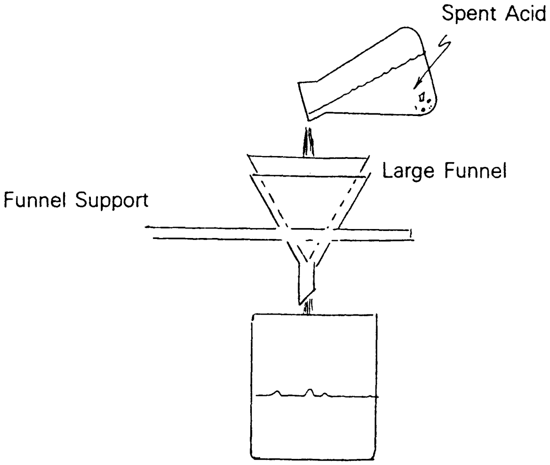


Figure 4.5. Filtering off spent acid

You now have a blue-green liquid, devoid of solid matter, in a large glass beaker. The liquid is a solution containing dissociated positive ions called cations. The blue-green color comes from the copper ions; the silver ions are colorless.

Step 3. Precipitate the silver as silver chloride. The trick is to drop the silver ions out of solution by selective precipitation—that is, by forming a chemical compound with the silver ions, leaving the copper ions behind undisturbed in the solution. To precipitate silver chloride, dilute the blue-green solution with three volumes of water (tap water) and add table salt (sodium chloride) or

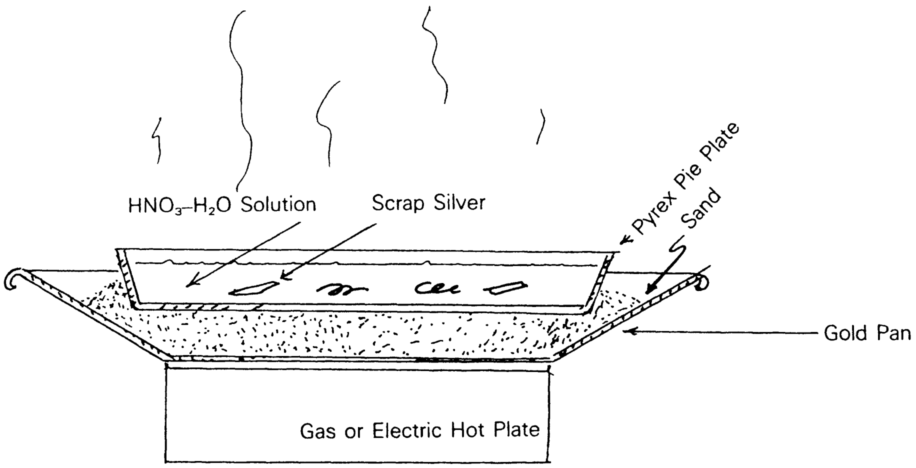


Figure 4.6. Simple sand bath setup

hydrochloric acid. At once, silver chloride (AgCl) starts to form as a white curdy precipitate.

Give the silver chloride some time to settle, and then take some of the solution from the top of the liquid with a bulb (ear syringe) and put a couple of inches of it into a test tube. Hold this in a strong, direct light and add a few drops of hydrochloric acid. Watch for a white cloud of silver chloride; if none forms, set your bulk solution aside to settle overnight.

If silver chloride forms in the test tube, you did not add sufficient salt or hydrochloric acid to your bulk solution to precipitate all the silver as silver chloride. If this is the case, throw in a handful of salt or add a couple of ounces of hydrochloric acid to the bulk solution. Let it settle, and then retest the top liquid in the test tube. When satisfied, let the bulk solution settle overnight.

You probably noticed that in the digestion operation, I said to use distilled water, but then switched to tap water to dilute the solution prior to adding salt and hydrochloric acid. The reason for this is that most tap water is chlorinated; if you used chlorinated water in the initial digestion of your silver, silver chloride would form on the surface of the scrap silver. Because silver chloride is insoluble in nitric acid, the reaction would then cease because of the insulating coating of silver chloride on the metallic silver. On the other hand, chlorine is used as a reagent in the precipitation of silver as silver chloride, so when you dilute your solution at that point, the more chlorine in the water the better.

Step 4. Separate the silver chloride from the solution containing the copper ions. You do this by carefully pouring or siphoning the liquid off as much as possible without disturbing the silver chloride or letting it become suspended in the solution.

Now wash the remaining solution and silver chloride off onto a filter paper in a Buchner funnel, with a vacuum assist setup. You can perform this operation without such a setup, but it will take forever.

The setup consists of a filter flask, a Buchner funnel, a single-hole rubber stopper for the flask and funnel, filter papers to fit the Buchner funnel, an aspirator (water) vacuum pump, rubber or plastic tubing, a safety bottle with hole and rubber stopper, and two "L"-legs (glass or plastic) to fit tightly in the safety bottle cork holes.

The Buchner funnel is a glazed ceramic funnel with a perforated plate on which the filter paper is laid. The paper should be no larger than the plate. See Figure 4.7. The filter flask is an Erlenmeyer-type flask with a side spud (connection) so that air can be sucked out of the flask. See Figure 4.8.

The aspirator filter pump is a water–Venturi device you connect to a water faucet; when water flows through it past the Venturi, a partial vacuum is formed that causes air to be sucked through the leg, which is attached to a small opening at the minimum diameter of the Venturi, thus producing a vacuum pump. See Figure 4.9.

The filter can be arranged for rapid filtering. See Figure 4.10.

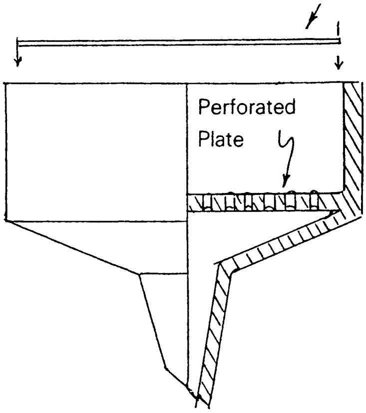


Figure 4.7. Buchner funnel (with filter)

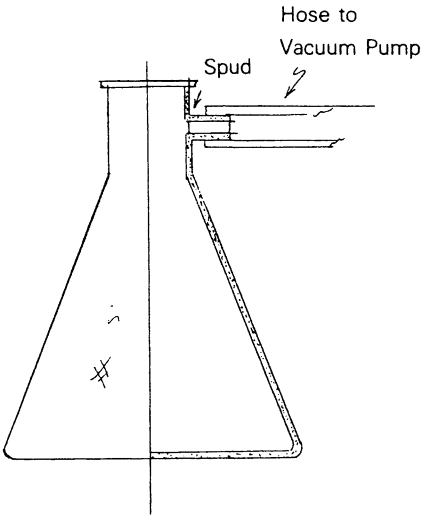


Figure 4.8. Filter flask vacuum

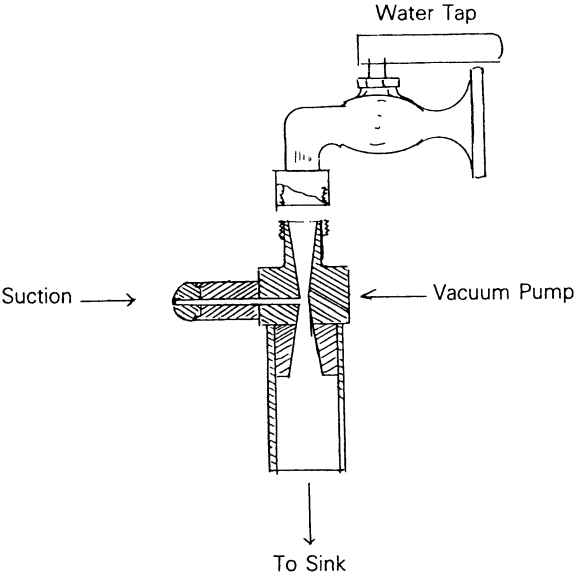


Figure 4.9. Water vacuum pump (cross section)

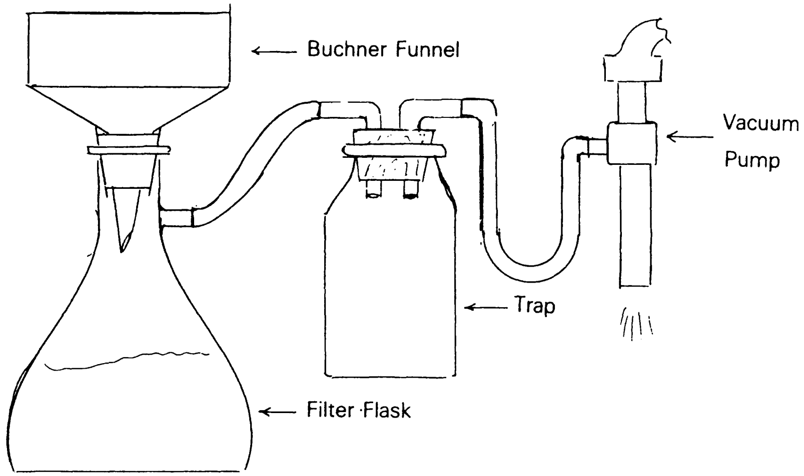


Figure 4.10. Rapid vacuum filtering system

When you select a filter paper, tell your supply house dealer what you are filtering (precipitated gold, platinum chloride, silver chloride, or whatever) and he will recommend from his line what would be best. There are so many types and textures that it would take several pages to cover them all.

Place the paper in the Buchner funnel and wet it down with a wash bottle so that it will stick tightly to the perforated disk. Start up the pump (water); you will hear it sucking and see the filter paper dimpling over the holes in the disk. If the suction is too great or if the filter paper is not fitted properly, the paper will break. Mix up a handful of wood, flour, and water, and practice with this. The trick to rapid correct filtering is to pour steadily into the funnel at the correct speed. You cannot just dump the material until the funnel is full; keep a little behind the action. Practice, and before long you will have it down pat. The purpose of the safety bottle is to prevent water from being sucked back into the flask by the pump if you happen not to be watching and allow the liquid in the flask to come up to the level of the suction spud on the flask.

After practicing, set up your filtering system and add enough water to your silver chloride to give it a thin, milk-like consistency; then, stir it well and pour a steady stream into the funnel (with the pump on). When you have ¼ in. of silver chloride on the paper (in the funnel), stop pouring and run hot water from a wash bottle onto this material until you have washed it free of any blue-green color. You have reached this point when the water entering the filter flask comes in clear and clean. If you do not wash the silver chloride free of the (blue-green) copper solution, the remaining copper will become part of your silver metal at the next stage.

Disconnect the tube from the flask. Remove the filter paper with the silver chloride on it and set it aside in a dark spot. Pour the liquid from the filtering flask into a large plastic container (with a top), called the stock pot.

Continue to filter and wash until you have separated all of the silver chloride. Collect this material from the filters, using a rubber spatula or wooden spoon, and put it into a plastic or glass container. When you have removed as much as possible manually, hold the filter by the edge and wash the silver chloride that is still clinging to it into the silver chloride container with the rest. The washed filter papers are put into another large, covered plastic container that is marked "Spent Filters."

Take a pinch of the silver chloride, place it in a clean test tube, and add enough strong ammonium hydroxide (ammonia) to cover it. Shake it, and the silver chloride should go into solution. If the solution is crystal clear, with no residue, the silver chloride is of high fineness. A white, undissolved residue indicates lead chloride or mercury chloride contamination.

If you do discover a white residue, filter it from the ammonia solution, place it in another clean test tube with water, and boil it. If it dissolves, it is lead chloride. If it does not dissolve, filter it off onto a clean filter and add to it a drop of strong ammonia. If it turns black, it is mercury chloride. Now, into the clear ammonia solution in which the silver chloride is dissolved, drop nitric acid, drop by drop. When the solution becomes acidic, the silver chloride will precipitate again.

Step 5. There are several good ways to reduce silver chloride to metallic silver: direct reduction, reduction with zinc, and reduction with iron.

Direct reduction is a one-step process of reducing silver chloride to metallic silver. The reduction is accomplished by heat and a reducing flux.

Set the silver chloride aside in thin batches to dry. Mix equal parts (by volume) of dry borax, lead-free glass, and soda ash; this is your reduction flux. Now mix the dried silver chloride with an equal volume of flux. Put the mixture into a graphite or fused silica crucible, filling the crucible less than half full. Put the crucible in a crucible furnace and melt down the mixture, slowly at first, then with increased heat.

Watch the crucible carefully. Its contents will bubble and have a tendency to boil over; reduce the heat whenever necessary. When the material in the crucible settles down, add a small amount of the flux and silver chloride mixture. Repeat this procedure each time a new addition settles down. When the crucible is about three-quarters full and its contents are not bubbling, pour the contents into a dry cast-iron bullion mold, slag and all.

When the mold has cooled, dump out its contents. Break off the slag by tapping it with a small ball-peen hammer. Examine the slag for silver shot (fine silver BBs) that did not sink all the way through the slag formed by the flux during reduction. The slag should be glass-like, brown to apple green. If the slag is gray and has white speckles, the reduction was incomplete: the white is unreduced silver nitrate and the gray is incomplete flux and metal reduction.

You can easily check a small portion of questionable slag on a charcoal block with the blow pipe. Crush the slag and mix it with some of your finely powdered reducing flux. Dampen the mixture and make a small ball; then heat it with a reducing flame. If your previous reduction was incomplete, you will at this time reduce a small silver bead out of the slag under the blow pipe. Of course, if the slag is carrying free silver BBs, you have little choice but to crush the slag and recover the metallic silver by panning or by using a Dam machine (wet centrifugal separator). Examine the floor and walls of the furnace and the outside of the crucible for free silver BBs. If you find that there is a large silver blob in the furnace bottom, you had a boil-over that you missed or a silver nitrate flux mix that got spilled. This type of reduction is tricky: the chlorine fumes are terrific, and the operation requires great skill to prevent the loss of silver values.

If, by chance, you use a standard clay melting crucible, you will make this mistake only once. The silver chloride, when it becomes liquid, will seep through the crucible's wall just as if it were a sponge, and the silver that does not go up the flue will be reduced in the furnace and on the outside of the crucible. See Figure 4.11. The silver from direct reduction is always of doubtful purity.

Reduction of silver chloride to metallic silver with zinc is easy to do with little loss of silver. It is my favorite method.

Assume that you have washed the silver chloride free of all blue-green stain, using lots of hot water; in doing so, you have also gotten rid of any lead chloride that was present because it is soluble in hot water. Some operators like to dry the silver chloride out completely before beginning this treatment. I find this a waste of time—the silver chloride, when dry, is difficult to wet and break up.

Place the silver chloride in a shallow glass or glazed evaporating dish (you can use a Pyrex pie pan if you like); spread it out so that the material is about

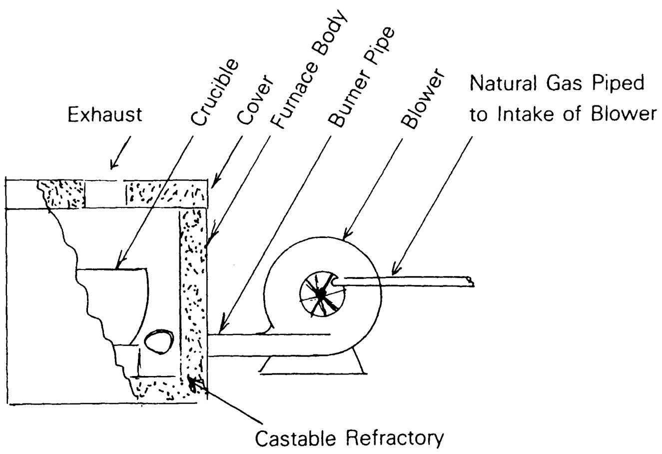


Figure 4.11. Basic crucible furnace

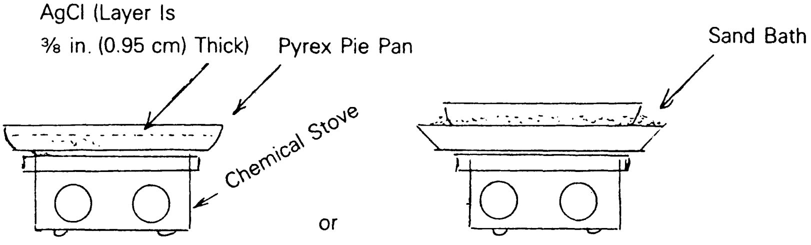


Figure 4.12. Cementation of silver chloride (first step)

⅜ in. thick. Then place the dish on the chemical stove or on a sand bath on the gas hot plate. See Figure 4.12.

Cover the silver chloride completely with a mixture of 1 part sulphuric acid (H_2SO_4) and 15–20 parts tap water; stir this well with a plastic or wooden spoon, and warm slightly. Now add some zinc shavings or mossy zinc. At once, the zinc will start to dissolve in the acid solution, giving off hydrogen bubbles. As the zinc dissolves, the silver chloride in contact with it is reduced to metallic silver. The trick, therefore, is to keep stirring so that every particle of the silver chloride makes contact with the dissolving zinc and is reduced to metallic silver.

You can use zinc powder, zinc shot, or zinc plates as your zinc source; however, mossy zinc or zinc foil works fastest. It takes a ¼–½ lb. of zinc and ½ lb. of concentrated sulphuric acid to reduce 1 lb. (dry weight) of silver chloride. When the reaction starts, you can discontinue warming. When reduced, the silver chloride goes from white to a gray granular silver that looks like cement and is called cement silver. Examine some of it in the spoon. Put a small sample of it on a hard surface and rub it with a burnisher: It becomes bright silver flakes. See Figure 4.13.

When, upon examination, you find no white, unreduced silver chloride in the dish, pour off and discard the liquid. Pick out any visible pieces of undissolved zinc. Your next step is to free the cement silver from any undissolved zinc you

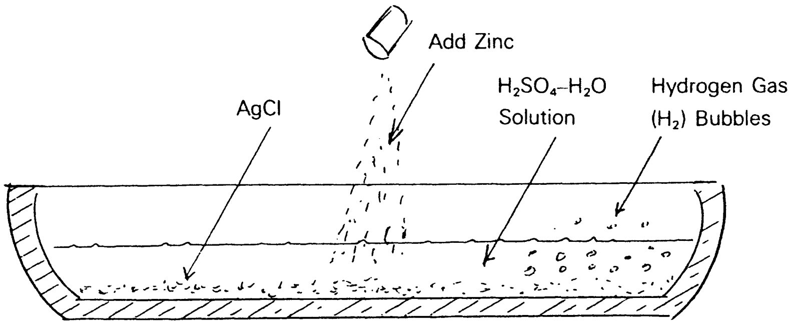


Figure 4.13. Cementation of silver chloride by ion exchange—silver for zinc

did not find. Mix together 1 part weak acid (hydrochloric or sulphuric) and 20 parts tap water, cover the cement silver with this, and stir well. Let everything settle down until it is calm and then look for bubbles. When you see no more bubbling, all the "tramp" zinc is in solution. Pour off this final acid wash and discard.

Wash the cement silver onto a filter in your Buchner funnel and rinse it with plenty of hot water. Use the vacuum to draw the liquid through. Then set the washed cement silver aside to dry. When dry, the silver can be melted with a little general melting flux (soda ash, borax, and lead-free glass) and cast into an ingot or bar. See Figure 4.14.

A third method of reduction is to use iron in place of zinc. Iron nails or washers work quite well. If you have only a small batch—3 or 4 ounces—of silver chloride to reduce to cement silver, do what I do: I cover the silver chloride with my 15-to-1 diluted sulphuric acid in a steel gold pan and work it around with a plastic automobile window scraper, getting all the silver chloride to touch the surface of the pan. The pan is the reactor in place of zinc or nails. This is a quick process. Remember, the dilute acid is dissolving the gold pan, and you can perform this operation only so many times in one pan before the pan becomes paper-thin.

I have reduced hundreds of ounces of silver chloride using nails; the iron is slower, but cheaper, than zinc. In addition, the leftover solution, which is iron sulphate, I evaporate in shallow plastic trays to recover the iron sulphate crystals. Ferrous sulphate or copperas ($FeSO_4{\cdot}7H_2O$) can be used to precipitate gold from gold chloride solutions.

Silver chloride can also be reduced using aluminum, copper, or other metals.

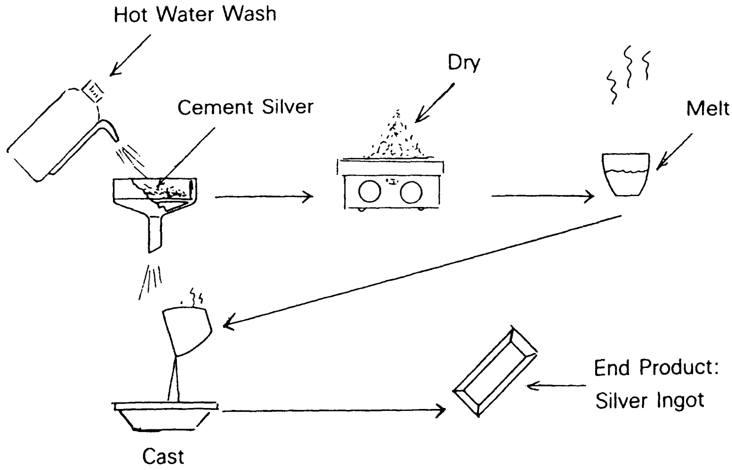


Figure 4.14. From cement to cast silver

Save all filter papers from every operation and place them in your container marked "Filter Papers."

You should perform the entire parting operation with very small pieces of silver, first pure, then sterling, in test tubes, before jumping to a large batch. Familiarity with the operation on a small scale will be very beneficial to you, and you will know what to expect at each step.

Refining Silver

Regardless of how your silver was brought into its separate, metallic state, it is of questionable purity and must be refined. You can go several ways, but the two basic systems are electrorefining in a Balbach–Thum electrorefining cell (also called a Moebius cell) and simply re-refining by wet chemical means.

You can simply melt the silver from your nitric acid parting operation, granulate it, and repeat the entire procedure. You can if you wish, when you reach the silver chloride stage this second time around, put the entire batch of silver chloride into solution with ammonium hydroxide. Filter this through a fine filter paper, precipitate it with nitric acid, and then reduce the silver chloride to cement silver. Dry silver chloride is approximately 75% silver by weight and 25% chlorine.

Another option is to redissolve the cement silver in nitric acid, prior to melting, at your first parting operation. Reprecipitate the silver as a chloride and then recement it. Any repetition of the process at any stage results in a finer, purer end product.

All solutions from your operations, except cyanide solutions and sulphuric acid solutions from the cementation operations, go into the stock pot.

Sterling silver is 92.5% silver melted together (alloyed) with 7.5% copper.

Coin silver is 90% silver and 10% copper.

Commercial silver is any silver 99.9% pure or purer.

Foreign silver can run as low as 70% silver and 30% copper.

Danish silver runs from 83% to 92.5% pure (the level of sterling silver).

Nickel silver (also known as German silver) is not silver but an alloy of nickel, copper, and zinc.

Gold and Copper Alloy

As another simple case, assume you have some clean yellow gold (copper and gold) scrap. The higher the purity of the gold, the more passive it is and the tougher it will be to separate it from an alloy—in this case, copper. The copper in the gold is called the base metal. This is what you want to part from the pure gold and dispose of.

As in the case of the silver–copper alloy, in order to part the gold–copper alloy, you must have a plan. See Figure 4.15.

Step 1. You must determine the average karat-value of the gold you wish to part and refine. If the gold is stamped 14kt, 10kt, or some other karat-value, as most gold jewelry is, you already know what you are supposed to have and can figure the percent of base metal from there.

If you multiply the karat mark by 4.16, you have the percentage, by weight, of gold. If a piece of gold is marked 14kt and you multiply this by 4.16, you find that the percentage weights are 58.24% for the gold and 41.75% for the base metal. Twenty-four-karat gold is pure (100%) gold, as you can see by multiplying the karat (24) by the karat factor (4.16). The product (99.84) rounds to 100 (%).

If the gold is not marked, check it with your set of gold needles. With the gold in question, make a short mark on a touchstone, a piece of unglazed porcelain, or a clean white Arkansas whetstone. Now, make a guess at the unknown gold's karat-value, say 14kt. On one side of the unknown mark; then, put a mark with a 12kt needle, and on the other side, a mark with a 16kt needle. Then place a drop of aqua regia on each of the three marks. See Figure 4.16.

Now watch the three marks dissolve. If the 12kt line dissolves first, then the unknown next, then the 16kt mark, you will know that the karat of your unknown

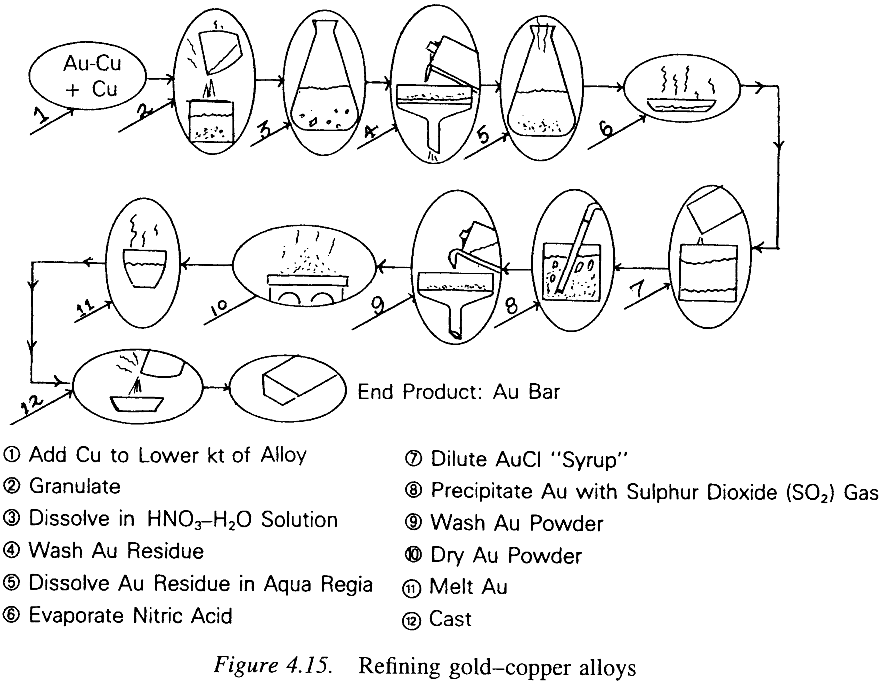


Figure 4.15. Refining gold–copper alloys

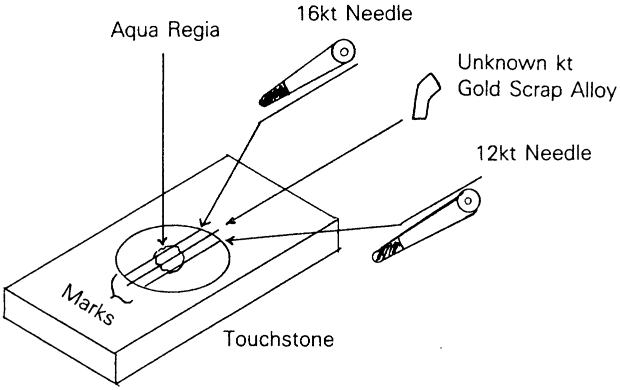


Figure 4.16. Using the gold needles and the touchstone

is greater than 12, but less than 16 (and therefore probably 14). If your unknown disappears before the 12kt mark does, it is of a lower karat than 12; conversely, if the unknown disappears last, it is of a higher karat than 16. By changing the needles, you can pin your approximate karat very close.

The less passive (that is, less resistant to digesting in an acid) the material you work with is, the easier your job is. It is much easier to part a small percentage of gold from a large percentage of copper than to part a large percentage of gold from a small percentage of copper.

The procedure you must follow is called inquartation. This means adding copper to the alloy you wish to part in order to lower its karat-value to 6kt or lower. At that point, the parting process becomes a copper proposition.

Step 2. Inquartation is the reduction of the karat of a given quantity of gold scrap to 6kt or below, so that three-quarters of the materials's weight is copper and one-quarter of it is gold. A low-karat gold is much easier to refine (extract pure gold from) than a higher-karat gold because the acids used in refining get at the base metals much more easily in the former case.

If you have 1 troy ounce of gold scrap that you figure averages about 12kt (some pieces being 10kt and some 14kt), how much copper must you add to reduce it all to 6kt or lower?

The formula for lowering the karat to 6kt is $A = \frac{G(K-6)}{6}$ where A is the amount of copper you need, G is the weight of your gold scrap, and K is the average karat of the scrap.

If you have 1 ounce (20 pennyweights) of gold scrap that averages 12kt, you have $A = \frac{20\ (12-6)}{6}$, or $A = (20 \times 6) \div 6$, or $A = 120 \div 6$, or $A = 20$. Therefore, you need to add 20 pennyweights (or more) of copper to your 20 pennyweights of scrap to get an inquartation equal to 6kt (or lower). Weigh your 20 pennyweights of copper—you can use clean copper wire or snippings from a piece of sheet copper.

Step 3. Place this copper in a hand crucible with the gold scrap and melt them together. When the mixture has become a very hot liquid, pour it, in a thin stream, into a large bucket of cold water from a height of at least 4 ft (just as you did in the sterling silver example).

Then (again, exactly as you did in the silver example), digest everything possible in nitric acid solution, carefully decanting off the spent acid solution so that you do not pour out any insoluble or undissolved material, and adding fresh acid. Do this in a beaker or Erlenmeyer flask with a spin bar, over low heat until the reaction starts, and with no external heat thereafter. When you reach the point at which, when fresh acid is added, there is no longer any visible action or brown fumes (nitrous oxide), let the solution cool, and then dilute it with distilled water by about three volumes.

If you did this correctly, most of the base metal is now in solution, leaving behind everything that is insoluble in nitric acid: the gold and any platinum-group metal except palladium. If, by chance, there was a percentage of silver in your copper–gold alloy (yellow gold), it is now in solution with the copper. To check, put a couple of inches of the green copper nitrate solution in a test tube, warm it slightly, and add to it a few drops of hydrochloric acid or a pinch of table salt; watch for a precipitation of silver chloride. If silver chloride does appear, proceed to separate the metallic silver; if not, carefully pour off and discard most of the liquid.

Step 4. The brown to black residue in the flask from the nitric acid digestion of your inquartated and granulated copper–gold material is nearly pure gold, with perhaps some additional metal of the platinum family.

Wash this material onto a filter paper in the filter funnel, with the vacuum pump on, and then rinse it—first with some dilute nitric acid (1 part acid to 10 parts water), and then with plenty of hot water. Next, remove the filter with the gold residue and set it aside.

Now check the washings (liquid) for any values. If they are barren, discard them; if they carry any values, add these to the stock pot. Place the filter under a heat lamp to dry the residue from the filtrate. Be careful that the filter paper does not catch fire.

Step 5. There are two approaches to dissolving gold in aqua regia. One is to cover the brown powdered gold from your previous step with aqua regia and boil it to dissolve it. Although this method works, the other method is much faster and uses less acid. In neither case should you boil the aqua regia, as this drives off the acids and is wasteful. Gentle heating is all that is necessary.

For the second method, make up some aqua regia (one part nitric acid, by volume, to three parts hydrochloric acid) and place it in an Erlenmeyer flask with a spin bar on the hot plate, which should be set to "Hot." Rotate the bar. Keep the aqua regia hot but below boiling. When it is well heated, speed up the bar and sift the dry gold residue (left from your nitric acid digestion, which removed the base metals) in small amounts into the aqua regia. The residue will go into solution almost instantly.

It is hard to say how much acid will be required per ounce of metal treated because you never operate at 100% efficiency, but experience shows that it takes about 5 or 6 ounces of acid per ounce of metal.

When the acid is spent and will no longer dissolve additions of the gold residue, pour the liquid off into another flask and add new aqua regia to the flask in which your dissolving operations are taking place. Repeat this process until you have put everything you can into solution. Now combine all your aqua regia solution into a single evaporating dish.

Step 6. If there is any residue from the aqua regia treatment, wash it off onto a filter and set this aside. Add the wash water to your aqua regia solution in the evaporating dish. If the aqua regia solution contains some gray to whitish sediment, this is probably silver or lead chloride precipitated by the hydrochloric acid in the aqua regia solution. Add 1 ounce of sulphuric acid per quart of liquid to the aqua regia solution in the evaporating dish. Boil this combined solution down slowly with a spin bar on the hot plate. Avoid overheating and spattering. The liquid disappears rapidly at first, but as the solution thickens, it evaporates more slowly and you have to watch the temperature to avoid spattering. The purpose of the sulphuric acid is to rid the solution of any lead, which will precipitate as a lead salt in your final solution.

Boil the aqua regia solution down until it takes on a syrupy consistency. Add some full-strength hydrochloric acid; you will immediately see the familiar brown fumes of nitrous oxide, as unused nitric acid is expelled. Boil the solution down to the thickness of syrup again, add more hydrochloric acid, and repeat.

You should do this at least twice, and preferably three times. The procedure rids your solution of unused nitric acid. As long as your solution contains free nitric acid, it remains an aqua regia solution, and an aqua regia solution, however weak, can hold gold ions in solution or redissolve gold that has precipitated out of solution. This is an especially acute problem when precipitates are involved: Being finely divided, precipitates are easy to redissolve in the presence of the right chemical agents.

This evaporation and reevaporation with additions of hydrochloric acid, as time-consuming as it seems, is one of the most important parts of the entire refining process. If you fail to do this correctly, you will find yourself with a large volume of (gold-bearing) solution that has to be evaporated, at a much greater expense of time. See Figure 4.17.

Step 7. When you are sure that you have driven off all the excess nitric acid, let the evaporating dish containing the syrup-like solution cool down. Wash the sides of the dish with a wash bottle to collect all the solution in the bottom of the dish. When it has cooled, wash all the solution from the dish into a large (tall) beaker or glass cylinder with the wash bottle. See Figure 4.18.

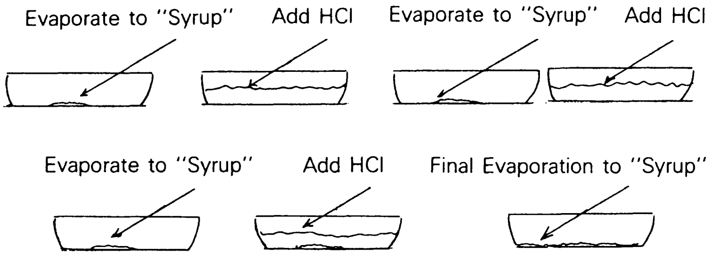


Figure 4.17. Triple evaporation of aqua regia

Dilute the solution with hot water to three or four times its original bulk, and let it stand—for several days, if possible. This will allow any silver chloride, lead salts, or metallic residue to settle out of the solution. The solution must be perfectly clear and free from any sediment. Any sediment that gets into the gold precipitate will contaminate the pure gold with other metallic elements. Pour the bulk of the clear solution off into a clean container (plastic if you choose), filtering the last part to catch any sediment. Clean out the large beaker or cylinder with hot water, and then pour the solution back, including the last filtered portion.

Wash the contents of the filter paper off into the stock pot and drop the filter paper into the used filter paper container. Look at the color of the solution; if it contains other metals than dissolved gold, such as copper or nickel, it will be a greenish brown. If gold is the main element, it will be a yellowish brown. If of very high quality, it will be a bright, clear yellow just as your gold standard is.

Place a drop or two of gold standard in a cavity of the spot plate, and in a cavity next to it, a drop or two of the solution. Add one drop of fresh stannous

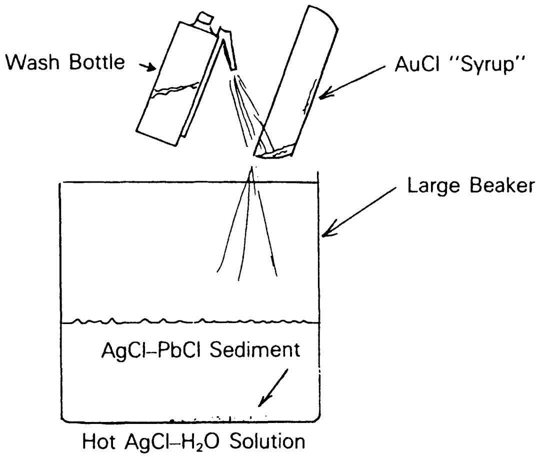


Figure 4.18. Diluting thickened gold chloride and settling out silver chloride and lead chloride

chloride testing solution in each; note the color change. Wash the contents of the spot plate into the stock pot with the wash bottle.

Precipitating Gold with Copperas

There are several ways to precipitate the fine gold from your solution, one of which is to use copperas (iron sulphate). You will need about 15 ounces of copperas to recover (precipitate) 2½ ounces of gold from solution.

Weigh out what you feel is enough copperas and add a 10% excess. Dissolve this in hot or warm water in another beaker. Add full-strength hydrochloric acid to the copperas solution, a little at a time, until the copperas solution turns a clear, apple green. Pour the copperas solution slowly into the gold solution while stirring with a glass rod. The gold will appear as a dark brown cloud. Let this cloud settle (usually overnight).

After it has partially settled, take a sample from the top of the solution with an ear syringe and put it into a test tube so that the test tube is filled to a height of at least 3 in. In good light, drop a large crystal of copperas into the solution; watch closely. If a brown cloud forms around the descending crystal of copperas, you have not used sufficient copperas solution to precipitate all the gold that was in solution. In that case, add more copperas solution to your gold solution. You should make the crystal test until you get no brown cloud. The solution from each test is poured back into your large precipitating cylinder containing the main solution.

Suppose that when you started pouring the copperas solution into your main solution to precipitate the gold, the commingling solutions generated bubbles and brown gas. This would be copperas reacting with free nitric acid that you had failed to get rid of in your triple evaporation of the aqua regia solution in Step 6.

If this is the case, you have only two corrective options. One is to start boiling everything down to a syrupy thickness again; but, because you have diluted the previous thick solution by three or four volumes, you are faced with a large volume of liquid to evaporate. The other option is to keep adding copperas solution until the nitric acid is completely exhausted in reaction with the copperas, and then add sufficient copperas solution to precipitate all of the gold. If you want to take this route, you should remove several ounces of the main solution and figure out how much copperas per ounce, pint, or gallon of the solution is required to rid the solution of nitric acid. Then you can decide which way is better.

I have seen the nitric acid condition so bad at this stage that when copperas solution was added to the main solution to precipitate the gold, the whole works boiled over, and the heat cracked the container. The key is to do Step 6 completely and correctly. This should also make you realize that, on your first attempt at it, you should only work down a few pennyweights of materials in order to familiarize yourself completely with what happens. Once you have become familiar with the whole process, you can make the jump to a larger batch (4, 5, or 6 ounces) of yellow gold with some degree of confidence. See Figure 4.19.

When you are satisfied that all the gold in the main solution has been precipitated and has sufficiently settled to the bottom, siphon off and discard the bulk of the liquid, being careful not to siphon off any of the brown power (the gold). Filter off the last portion, washing the gold powder onto the filter paper. With hot water from a wash bottle, wash the gold down well while the vacuum pump is running and the gold is on the filter. Remove the gold on the filter by washing it into a clean casserole dish (glass or glazed ceramic).

Wash the casserole dish ahead of time with lots of hot water and soap and rinse it several times with hot water. Do not touch the inside with your fingers. If the casserole dish is not completely grease-free, some of the gold during the next treatment can become greasy and float away.

When the gold has been washed into the clean casserole dish, fill the casserole dish with hot water. Stir, let the gold settle, pour off the liquid, and repeat. Now cover the twice-washed gold in the casserole dish with full strength hydrochloric acid, place the dish on the hot plate, and bring the acid to a boil. This hydrochloric acid treatment dissolves the light yellow mud that is mixed with the gold powder. This mud comes from the copperas.

Pour off and discard the acid; then wash the remaining powder again with hot water. Add a little more acid, pour off and discard it, and wash the powder with hot water twice. The gold should be clean and of a reasonably high fineness (99% pure or better). Wash this gold onto a filter in a glass funnel with the wash

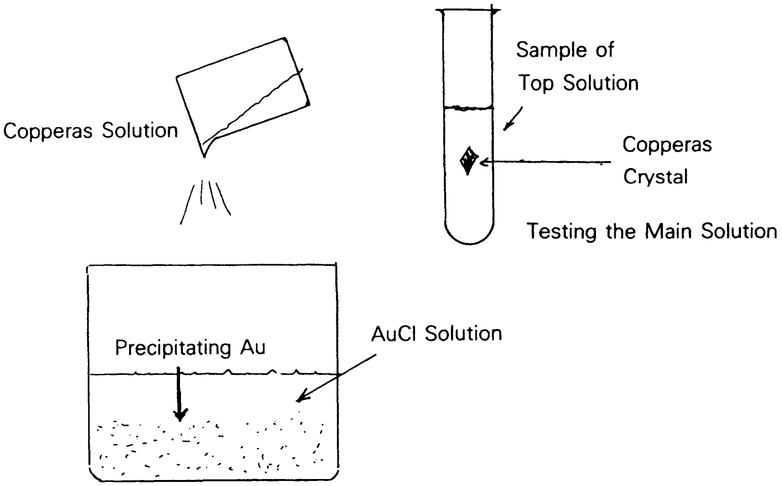


Figure 4.19. Precipitating gold from the mother solution with copperas; test for completion

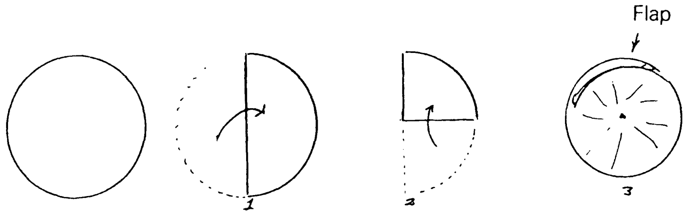
bottle and work the gold down into a single lump in the point of the filter paper. Let the gold partly dry in the funnel, then lift the paper and the gold out of the funnel, open the filter, and spread it out on a flat surface to dry. See Figure 4.20.

Rub the inside of a clay or fused silica crucible with a thin paste of borax. Place the dry gold powder in the crucible and cover it with a little borax. Melt the gold in the furnace or with a torch. When the gold is molten, add a pinch of saltpeter (potassium nitrate–KNO_3) from time to time. This will help to oxidize any impurities. The gold can be poured into a clean warm ingot mold or allowed to cool in the crucible, after which the crucible can be broken and the gold button removed.

If you have followed the parting steps closely, the gold should be of high purity. However, if because of faulty refining (parting) or for some other reason the button is not as pure as you desire it to be, you can roll it out thin and remelt it with borax and saltpeter as before; or, you can use ammonium chloride or bichloride of mercury in place of the saltpeter. Do not inhale the fumes from this melting operation: They are toxic. *(Work under a draft.)* See Figure 4.21.

This remelting operation is considered one of the repurifying operations.

The gold at this point is usually pure enough to sell; however, if it is carrying platinum-group metals or other impurities, it can be re-refined by repeating the wet procedure, starting with aqua regia and carrying through as outlined above, or it can be upgraded in an electrolytic cell.



Folding a Filter Paper

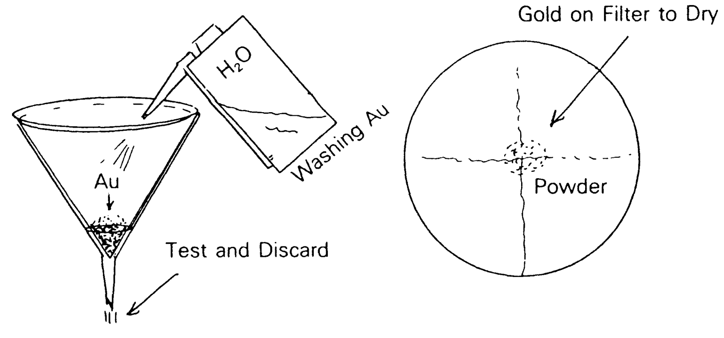


Figure 4.20. Final washing and drying of precipitated gold

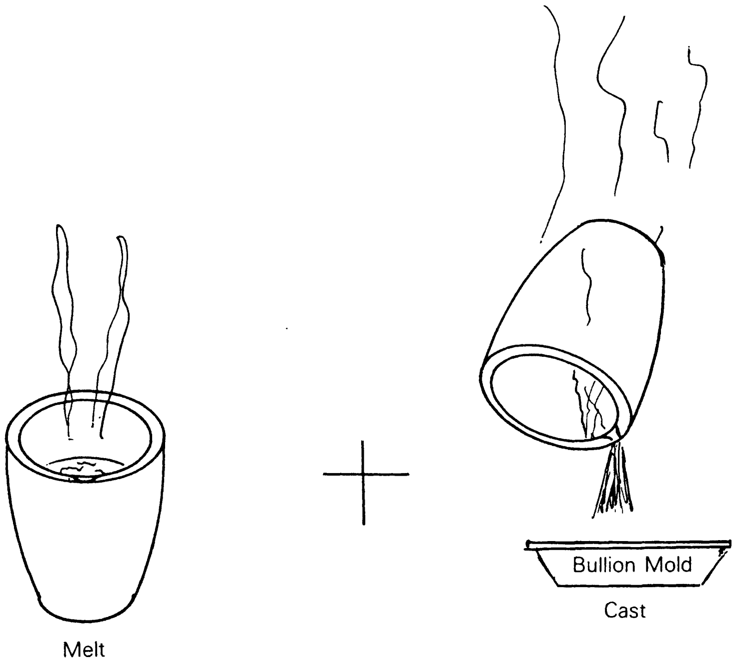


Figure 4.21. Melting and casting gold in a bullion mold

If you use copperas to precipitate gold from gold chloride, you have to contend with the addition of extra liquid and with the removal of the mud left by the copperas.

An alternative to copperas is sulphur dioxide gas. I prefer it: It is clean and does a good job of precipitating the gold. In addition, you do not have to test over and over to make sure you have used enough of it, as you do with copperas.

Sulphur dioxide (SO_2) is a colorless gas (or liquid) that has a sharp pungent odor. It is an outstanding oxidizing and reducing agent. It is noncombustible. It is toxic if inhaled and a strong irritant to the eyes and mucous membranes. Sulphur dioxide gas is used as a refrigerant and is readily available as a gas in cylinders containing 4 or 5 cubic feet of gas from chemical supply houses. The cylinders last quite a long time, as it does not take much gas to do the trick.

I have found that with sulphur dioxide (instead of copperas) as a precipitant, the gold refined is of higher quality; at any rate, sulphur dioxide is cheaper, easier to use, less bulky, keeps indefinitely until used, does a very good job of selective precipitation (is not likely to carry down any substances other than gold), and, in short, gives a very good separation. The process is quite simple: You start by boiling down the aqua regia to the thickness of syrup and adding hydrochloric acid; repeat this procedure two or three times, as you did before, diluting the final solution with three or four volumes of water.

Attach a rubber (or plastic) hose at one end to the tank valve, and at the other end of the hose, attach a suitable length of ¼-inch-diameter glass tube. See Figure 4.22. Now, assuming that you have removed the excess nitric acid from your solution and that the solution is clear of any sediment or cloudiness, you are ready to go.

It is best to have your solution in a tall container rather than a wide one, in order for the gas to make easy contact with all the solution. A tall glass cylinder is best: with it, you can see exactly what is happening. The "gas" within the sulphur dioxide tank is actually liquid (like propane); therefore, the tank must be kept upright or liquid will come through the tube into your solution. Make sure the tank is secured safely so as not to fall or tip.

Insert the glass tube into the solution so that the open end is near the bottom. Crack the valve very slightly so that some bubbles come up through the solution. The first bubbles will be absorbed. Now adjust the valve until you are getting about one bubble per second. Watch the solution. When it starts to become dark with precipitated gold, slow down the gas flow slightly.

Stir the solution with the glass gassing tube to bring all the liquid in contact with the gas bubbles. If you have, for example, 5 ounces of gold in a gallon or so of solution, it takes about 25 min of bubbling to precipitate all the gold out of solution. As I explained in the case of precipitating with copperas, if the solution is not free of nitric acid, you will be unable to bring and keep all the gold out of solution. The best indicator of nitric acid at this stage is the presence of brown nitrous oxide fumes. If this is the case, you can reevaporate the solution as before, or simply keep gassing until all the nitric acid has been expelled; then, with additional gassing, the gold will come down.

If the gold fails to precipitate soon, and you suspect that the liquid is too high in acid content, you can remedy this by diluting the liquid with considerable water or by adding pinches of sodium bicarbonate, stirring well between pinches.

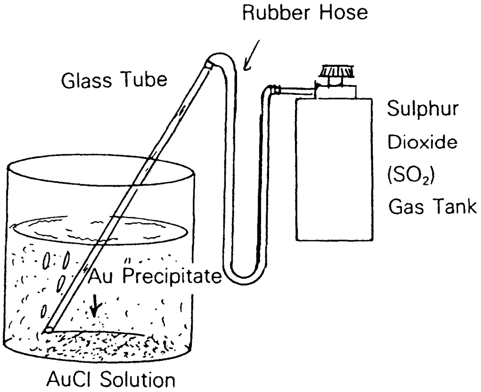


Figure 4.22. Precipitating gold with sulphur dioxide gas

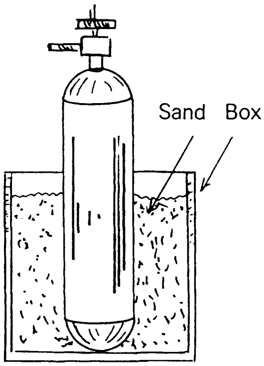


Figure 4.23. Safe way to use lecture bottle of sulphur dioxide

You can establish the best pH point with a sample of your solution, and then stay with that figure the rest of the way.

Let the gold settle, then check a sample from the top of the solution with stannous chloride for gold and with DMG for platinum metals. When the powder has settled, pour off most of the liquid, and filter off the last, washing the gold powder off onto a filter paper. Wash this with hot water. Wash the gold into a casserole dish and boil in hydrochloric acid to pick up any residual copper or other base metal. Wash it free of acid, dry it, and melt it as usual. See Figure 4.23.

A problem you can run into with sulphur dioxide is, because gas is a refrigerant, it is quite cool; if the gassing is done too rapidly, the valve on the sulphur dioxide tank can ice up (freeze) and jam, making it impossible to turn off. A rag soaked in hot water and wrapped around the valve will prevent this or unfreeze a frozen valve. Small lecture bottles can be held under a hot water faucet if frozen. Once you have used sulphur dioxide as a precipitant, you will probably use no other system. However, you should be familiar with other methods.

Precipitating Gold with Sodium Nitrite

Sodium nitrite ($NaNO_2$) is a chemical cousin of sodium nitrate (saltpeter) which we use as a flux. Sodium nitrite has a limited shelf life and will lose its strength on long standing. However, if used to precipitate gold, it will not contaminate the gold when melting, even if it is not washed completely out of the gold powder. It is also inexpensive and simple to use. The gold solution is worked down and diluted as usual, and you will have the usual problems if you do not expel all of the nitric acid. When using sodium nitrite, you want your solution to contain no more than 5% acid. If the gold fails to precipitate, dilute the solution and/or add pinches of sodium bicarbonate to neutralize some of the acid.

At the outset, you have two choices: You can simply add the sodium nitrite as a solid (powdered or in lumps) or you can dissolve it first in some warm water. Add a little of it at a time while stirring. The gold will precipitate as a yellow to brown powder. When the gold starts to appear, add a pinch of excess sodium nitrite. Allow the gold to settle. If it seems to be settling too slowly, add some hot water; this will speed up things. When the powder has settled, test the top solution for values; if there are none, discard it. Filter the last liquid and the gold onto a filter paper, wash the gold as usual, and melt it.

It is handy to keep some sodium nitrite in a dark, tightly closed container to use for small precipitations in testing or for small wet assays.

Precipitating Gold with Oxalic Acid

Oxalic acid ($CO(OH)_2 \cdot 2H_2O$) is a toxic white crystalline powder. Using oxalic acid as a precipitant has the disadvantage that both your aqua regia gold solution and the oxalic acid solution must be boiling. It is also more expensive than other methods. Oxalic acid is usually used with small batches of solution that contain fairly high-quality gold, free from most base metals. Its use is usually considered a repurification-by-precipitation operation. For example, if we took gold powder that had been precipitated with sulphur dioxide and redissolved it in aqua regia, boiled it down, and so forth, and then reprecipitated it with oxalic acid, this would be considered a repurifying or upgrading move.

Repurification is simply a repeat operation with variations, such as changing the reagents or methods of precipitating the second go around. This applies to gold, silver, and metals of the platinum family and is where electrorefining or electrowinning comes in.

Oxalic acid will not introduce any iron (as copperas can) or other material to the fine gold and will not contaminate the gold during melting. Refining requires about a troy ounce of oxalic acid per troy ounce of gold in solution. Remember that this particular method is done boiling hot, so be careful and use strong glassware. Do not attempt to use oxalic acid cold unless you wish to wait days for the gold to precipitate. Always make sure you have expelled the nitric acid from your aqua regia. Not carrying out the initial evaporation and reevaporation of the aqua regia solution correctly is the source of many of the problems people have with extraction and repurification, and it is really inexcusable.

Dissolve the oxalic acid crystals in hot water and add a teaspoon or less of ammonium hydroxide (ammonia); then, stir the solution. It should have no odor of ammonia. If it does, you added too much, so add some additional oxalic acid until you do not smell the ammonia.

Place the gold solution on one burner and the oxalic acid solution on another, and bring both to a boil. Now pour the boiling gold solution slowly into the boiling oxalic acid solution. If everything is right, the gold will precipitate at once. You then treat the gold powder as usual.

Metallic Precipitants

The use of base metals to precipitate precious metals is called cementation. Usually, it is used when you simply wish to recover precious metals from a solution without regard to their resultant purity. Normally, you would subject the metallics produced by cementation to further parting and purification.

The principle underlying cementation is the fact that a less noble metal, when introduced into a solution in which it is soluble and in which a more noble metal already exists in dissolved form (that is, as positive ions), will go into solution while all the ions of the more noble metal (or metals) will precipitate out in metallic form. This ion exchange depends on what is called the electromotive series.

An electrical potential difference exists between the two metals, one in solution as an ion and one introduced in metallic form; this potential difference, in effect, produces a miniature electroplating action.

Because each metal has a different electrical potential, each is either more positive or more negative than any other one. If you had a silver salt in a balanced solution (silver nitrate solution), for example, and you dipped a clean sheet of copper into this solution, a part of the copper sheet would enter the solution, displacing some of the silver, which would, in turn, be deposited on the copper as metallic silver. The copper, being (relative to silver) negatively charged, acts as the cathode of this miniature plating cell, and the silver, with its higher positive charge, acts as the anode; for this reason, the silver ions are drawn to and deposited on the copper.

This would also be true if the silver ions were in a cyanide solution, as dissolved silver cyanide. The silver ions would be precipitated as metallic silver, and copper would go into solution, taking the place of the silver in what was now a copper cyanide solution.

I spoke earlier about relative positive or negative electrical potential. Consider copper and silver. Copper's single potential towards solutions with normal metallic ion activity is +0.34 V and silver's is +0.80 V. Both are positive, but silver's is higher than copper's by 0.46 V; therefore, the silver functions as the anode. If the situation in the above example had been reversed, so that the copper was originally in solution as copper ions and a clean piece of silver had been dipped into the solution, the copper would remain in solution unchanged. In order to get a metal (in its metallic form) to exchange with the copper ions in solution, you would have to use a metal of a lower positive electrical potential—that is, a less noble metal—as the cathode, at which point the copper ions in solution would act as the anode and the copper would cement to the cathode. Iron would work well: Its electrical potential is –0.44 V.

Because zinc has one of the lowest electrical potentials among metallic elements (a single electrical potential of –0.76 V), it is a very useful tool for many metallic precipitation operations. Zinc is very widely used to precipitate precious metal values from cyanide solutions in both primary and secondary extractive operations.

If you have only one or two types of metallic ions in solution, this system can be of advantage. By adding zinc to an acidic or basic (cyanide) solution, you can precipitate the metallics, and then separate them from each other and from the undissolved zinc by selective digestion and precipitation. However, this system is slow at best. If you have a sizable number of different types of metallic ions in solution, your end product of cementation is going to be a complex of metals all mixed together, which you will have to part and refine individually anyway. If you used selective precipitation, rather than cementation, you could bring each metallic element out of solution separately.

Gold Scrap: Special Cases

Although the examples given above, step by step, have covered the simple case of parting an alloy composed entirely of gold and copper, you will encounter scrap gold in many forms that may require somewhat different methods of parting and refining.

Green gold scrap. Green gold is an alloy of gold and silver in which the percentage of silver may be as high as 25%. Aqua regia does not put metallic silver into solution but simply converts it into silver chloride, which coats the outside of the green gold, stopping the action of the aqua regia on the gold. The only way you could put green gold into solution in aqua regia is by continually scraping off the film of silver chloride as it formed, thereby exposing fresh gold to the aqua regia—an impossible task. Green gold has too high a gold content to yield to nitric acid and too high a silver content to yield to aqua regia. What you have to do is perform an inquartation with enough base metal (copper or zinc, for example) to lower the gold's purity to 6kt or lower, then remove the silver with nitric acid, and then remove the gold with aqua regia.

Alternatively, you could add enough fine gold to the gold–silver alloy to drop the silver content below 10%, granulate the alloy, and then digest it all in aqua regia; or you could add enough silver to lower the gold percentage to a point at which the whole alloy would yield to nitric acid.

Low-grade scrap. Rolled-gold, gold-filled, and gold-plated scrap, and gold scrap containing soft solder (tin/lead solder) will, at best assay 5% gold; electroplated gold will assay an even lower percentage. This kind of scrap can collectively be called junk, cheap, or low-grade scrap.

It is extremely difficult to separate gold from waste material profitably in the case of low-grade scrap, unless you operate on a large scale and purchase the scrap extremely cheaply. In many cases, precious metal refiners who buy low-grade gold scrap simply resell it to a copper refinery, which treats it as impure copper; the gold and silver become by-products of the copper refining operation. A large percentage of industrial electronic scrap falls into this classification.

If you accumulate relatively small amounts of gold-filled scrap (eyeglass frames, for example), use the scrap in inquartations, to lower high-karat scrap to 6 kt or below; in this way, you pick up some extra values you would not get by doing the inquartation with pure copper. Inexpensive gold-plated and gold-filled jewelry can be stripped of their gold in a cell filled with almost pure sulphuric acid [1 gal of pure sulphuric acid (H_2SO_4), 6 fluid ounces of distilled water, and ½ fluid ounce of glycerine]. The cathode is metallic lead. The gold layers to be stripped act as the anode. The correct electromotive force is 6 V DC at room temperature. See Figure 4.24.

In the operation of stripping gold plate with an H_2SO_4 electrolyte, the gold does not go over or adhere to the lead cathode but simply flakes off and settles to the bottom of the tank, from which it is recovered from time to time. This system is extremely fast, requiring only a few seconds of time per item. Very little of the base metal will go into solution.

For stripping silver plate, this method is much slower. The electrolyte should be 90% (by volume) sulphuric acid and 10% (by volume) nitric acid—as water-free as possible. If water gets into the electrolyte, the base metal will dissolve considerably. The anode here is the item being stripped; and the cathode is either lead or stainless steel. The bath is operated at 160°F. The silver goes into solution, rather than plating across onto the cathode. You recover it by precipitating it as silver chloride with sodium chloride or hydrochloric acid.

Remember, with low-grade gold scrap, you must handle large quantities of material for a small yield; if you are not equipped to handle bulk material and process it very cheaply, you cannot operate successfully. My opinion is: If you have lots of copper carrying a little precious metal, you are in the copper refining business; if you have lots of precious metals carrying small amounts of copper (or other base metals), you are in the precious metal business.

Gold scrap containing lead solder. Any time lead solder is present in gold scrap, even though the scrap may be high in precious metal value, it can cause serious problems.

Examine your material carefully prior to any melting or inquartation. Take

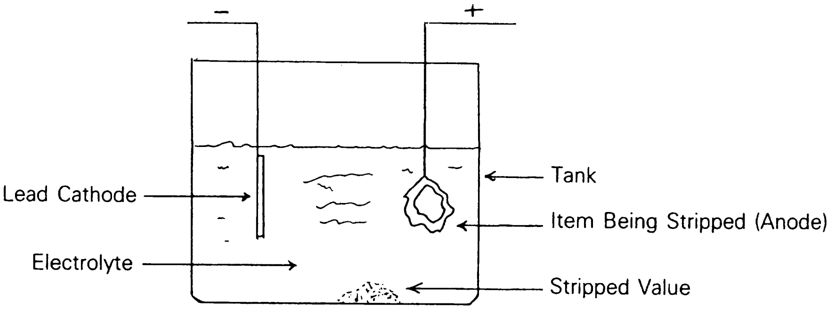


Figure 4.24. Simple electrostripping cell

pieces that have visible soft solder on them and boil them in full-strength hydrochloric acid until the solder loosens and can be scraped off. Discard this acid and wash the material completely free of acid. Lower the purity of the remaining material to 6kt or lower (if it is not already that low) and granulate. Digest as much of the granulated material as possible in nitric acid (one part acid to one part distilled water).

Any tin from the soft solder (tin/lead solder) that is left on the material will be converted into a tin paste, called metastannic acid; you can easily recognize it as a gelatinous, gooey paste. It would be helpful to dissolve a small piece of pure tin in hot, strong nitric acid in a test tube as a familiarizing exercise.

When the tin is immersed, the solution gives off brown fumes (NO_2), and the tin goes to pieces, without dissolving in the acid: The acid converts the tin into a white, pasty or slimy substance (metastannic acid). Any lead present will be converted to a white lead nitrate salt; however, because lead nitrate is highly soluble in water, you can remove it easily by diluting the nitric acid with water, thus putting the lead salt into solution with the base metals.

Dilute the nitric acid with hot water and pour this liquid off. Repeat the nitric acid digestion of your material, if necessary. Discard the dilute acid. Now wash the residue with lots of hot water and pour this off (watch for gold floaters). The residue will be a mixture of gold, tin paste, and any base metal that escaped the nitric acid treatment. Do not let this dry; put it in a casserole dish or evaporating dish and cover it with a solution of one part sulphuric acid to one part water (by volume) and warm. This will dissolve the tin paste along with any free tin. Pour this off, residue and all, into a large volume of water.

When the residue settles, decant and discard most of the liquid. Filter off the last of it, washing the residue onto the filter, and wash the residue with lots of hot water. The residue is now ready for digestion in aqua regia. I prefer to segregate any material that has soft solder on or in it and treat it as a separate batch.

White gold. There are two basic types of white gold: Expensive white gold is an alloy of gold and palladium, and inexpensive white gold is an alloy of gold and nickel. Probably 99% of all white gold you will ever see is nickel–gold, the cheap stuff. However, some white gold scrap for dental work (such as bridge work) contains palladium and/or platinum as the whitener; this may also be the case with fine, high-quality jewelry mountings.

The simplest test for distinguishing nickel from palladium or platinum in white gold is to make enough of a mark on your streak test stone with the unknown white gold to leave some metal particles on the stone. Add a drop or two of nitric acid or aqua regia. When the mark is dissolved, add enough ammonia, drop by drop, to neutralize the acid, and put a drop of your DMG (dimethylglyoxime) test solution on the neutralized solution. If the whitening metal is nickel, you will get a bright rose red precipitate.

Some jewelry and dental white gold carries nickel with palladium. You can do a double test for these elements in the spot plate. Place a small quantity of filings in the spot plate cavity, and dissolve these in a few drops of aqua regia. Add a drop of DMG. If palladium is present, you will get a copious precipitate that is bright canary yellow. Add ammonia, drop by drop, until the test smells of ammonia; if nickel is present with the palladium, the yellow will have been replaced by rose red (the nickel indication).

Platinum will give a yellow to brown test color when put in stannous chloride test solution. Remember to check your stannous chloride solution against your standard gold or platinum. Once you have identified exactly what you have, the choice of which way to go is simple. If it is mostly nickel-alloy white gold, you simply treat it as you would a gold–copper alloy. Lower the metal's gold concentration to 6kt or lower, granulate the metal, add nitric acid or aqua regia, and precipitate, melt, or repurify. If the metal is a gold–platinum or gold–palladium alloy, you should treat it as a platinum alloy.

Much is to be gained by separation and identification, and by refining each identified lot with the best method for the particular alloy or group into which it falls. Once you have identified a binary alloy as copper and gold only, or platinum and palladium only, you have a simple task ahead of you. Pinning down exactly what you have, separating everything according to its pedigree, and working each separately will save considerable time, chemicals, and effort. The methods of identification described here are generally rapid, simple, and fairly positive; this is not always the case, but you should take advantage of them whenever practicable.

Gold and complex gangue. When you obtain a batch of dental or jeweler's scrap, you often find it mixed with and attached to sand, glass, porcelain, or enamel. In some cases, melting and fluxing will accomplish a separation of the values, but not always. The enameled front on a gold tooth, for example, can be extremely difficult to break loose, and you can never get a complete separation.

The best method is to put the enamel, sand, or porcelain containing the gold scrap into a lead dish on a sand bath and cover it with hydrofluoric acid. This acid is a water solution of hydrogen fluoride (HF), a colorless, fuming, mobile liquid or colorless gas that is highly soluble in water. The hydrofluoric acid is warmed, and the material is stirred with a piece of platinum, gold, or hard rubber until the gangue is dissolved. See Figure 4.25.

Hydrofluoric acid is a dangerously strong, very corrosive acid: It can be very injurious if it comes in contact with your lungs or skin. Work under the hood and heat it carefully. The fumes will etch (frost) your glassware and windows. It is kept in plastic containers and used to be sold in wax bottles which then had to be kept in the refrigerator—a real problem. Usually, hydrofluoric acid can be used to treat several separate batches of material before it is spent. The used acid should be put in a separate plastic bottle and marked "used once," "used twice," and so forth, until spent; it is then diluted and disposed of.

Chrome plate. On occasion, you may encounter low-karat silver or white gold jewelry that has been chrome plated. It is almost impossible to dissolve

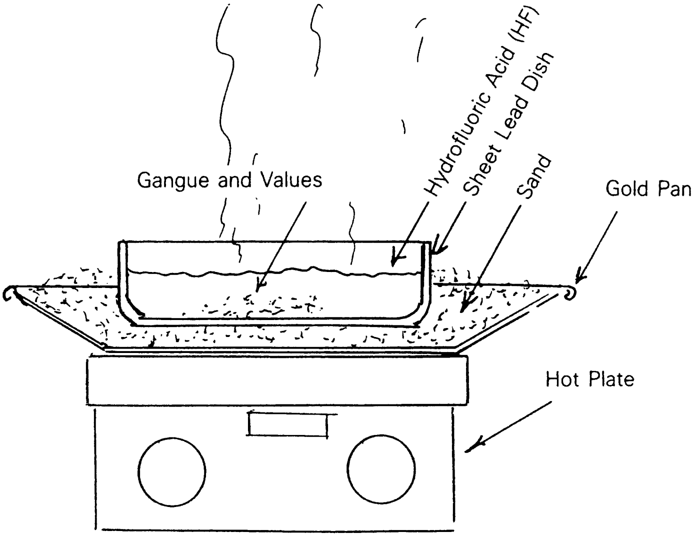


Figure 4.25. Dissolving gangue with hydrofluoric acid

chrome plate in nitric acid; it is also easy to mistake it for white gold. However, the chrome is easily dissolved in hot hydrochloric acid or in dilute sulphuric acid. If you get a little residual chrome mixed with your values at the aqua regia dissolving step, it will (if not in excess) not cause any problem.

Chrome plate can be stripped in a plating cell, too, using sodium hydroxide solution (NaOH) as the electrolyte and stainless steel as the cathode at room temperature. The electrolyte should be at a strength of about 90 g per liter of water.

Precious metals combined with emery or Carborundum™. If mixed with precious metal filings or dust, emery or Carborundum presents a real problem; neither is likely to be soluble in a single acid or base, although some emery polishing rouges and papers will yield to a strong solution of sodium hydroxide (lye).

Your best bet is to try to pan the emery or Carborundum off with the gold pan or to melt the filings into a button, granulate it, and dissolve everything in aqua regia.

Green gold and platinum combinations. Some jewelry consists of a green gold bottom and a platinum top or plate, welded together. You can handle this material in one of two ways. First, you can inquartate it with enough brass or copper scrap to allow you to part it as usual with nitric acid. Second, you can set up a simple electroplating cell, and plate the gold onto a copper cathode in a cyanide bath, leaving the clean platinum behind. See Figure 4.26.

The plating bath consists of 4–8 ounces of sodium cyanide per gallon of water. Use caution when handling cyanide and keep the solutions away from acid. The bath temperature should be 150°F, the voltage 8–10 V, and the amperage very

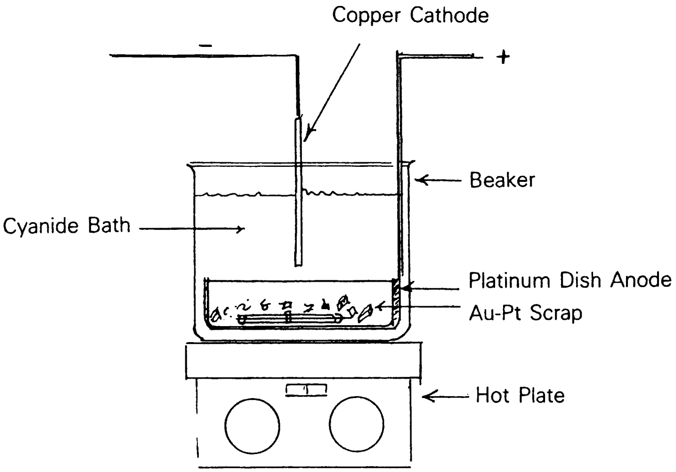


Figure 4.26. Parting platinum and gold with an electrolytic cell

high. To prevent flakes of gold that have formed on the cathode from falling back into the dish, make a cotton catcher using two embroidery hoops. This system can work while you sleep: Let it run all night. It is slow but effective.

Another method is to use a stainless steel container with a spin bar and a carbon cathode isolated in a porous clay crucible from the main bath. In this system, the gold, copper, and other metallic elements in the scrap that go into solution in the outer solution will stay there because their ions are too large to get through the barrier to the cathode; the current, however, will flow through. The outer solution is stripped of its values by metallic zinc cementation. The platinum or palladium values stay in the bottom of the stainless steel container because they are insoluble in cyanide. See Figure 4.27.

The bath can be composed of 4–8 ounces of sodium cyanide, just as the simple cell is. In either type of cell, you must check for free cyanide. I have worked with cells containing up to 12 ounces of cyanide per gallon of water—rather strong but fast working. With either cell, you will have to strip the bath of metal ions. With the isolated cathode setup, you can remove the pregnant solution and plate out the values in a separate cell. See Figure 4.28.

In the simple cell, I use steel wool to collect the values. The steel wool is then dissolved in a 1-to-15 solution of sulphuric acid and water to recover the values, but **beware:** You must be positive that you have washed the steel wool and its accompanying precious metals completely free of any trace of cyanide prior to dissolving it in the acid bath. *If you fail to do so,* you will generate deadly cyanide gas.

The mud containing the gold or other values is then washed with hot, 1-to-1 sulphuric acid and water solution to ensure that you did not miss any of the steel

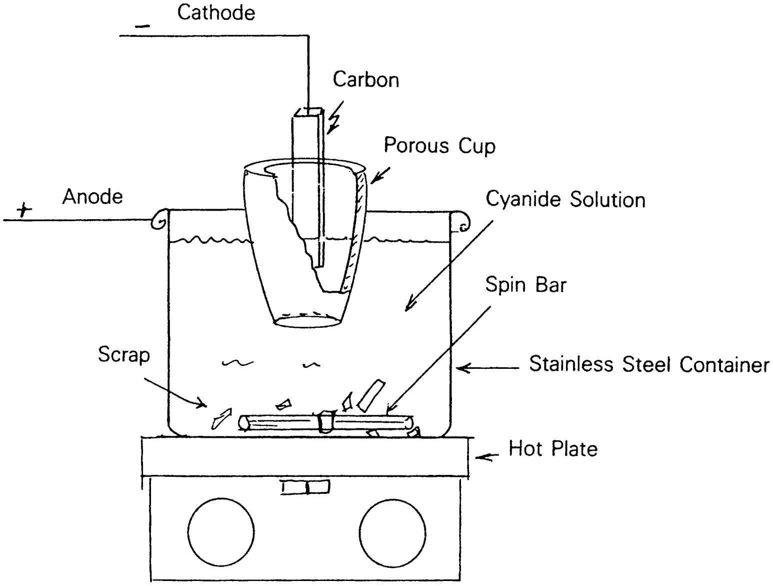


Figure 4.27. Parting cell equipped with isolated cathode

wool, and then in lots of hot water. Filter the mud onto a filter paper and set it aside to dry. The mud is then ready to part and refine by usual methods.

The platinum and palladium, once freed from the green gold or yellow gold, are washed in a little hot 1-to-1 nitric acid and water solution. Then they are washed with hot water and run off onto a filter to dry. As with all other acid solutions used in refining operations, a few drops of the nitric acid solution are tested for gold, silver, and platinum-group values with stannous chloride and DMG testing solutions; if any value is indicated, the entire acid solution is poured into the stock pot.

Another warning about cyanide: Cyanide is fairly unstable and will decompose very rapidly at temperatures above 150°F. At the boiling point, it decomposes very fast, going to ammonia and sodium formate. It is stable at temperatures below 115°F; however, to get anywhere with it in a plating cell or extraction cell, you have to heat it to 150°F. The smell is very much like almonds and is nauseating to most people. At any rate, do not breathe the fumes; work under the hood.

Spent cyanide solutions are a problem to dispose of because of their toxicity, despite the fact that cyanide is an unstable chemical that decomposes naturally over time.

You can render spent solutions that contain cyanide innocuous by diluting them with a large volume of cold water, adding an excess of sodium hypochlorite ($NaOCl \cdot 5H_2O$), and keeping the solution on hand for 24 h before disposing of

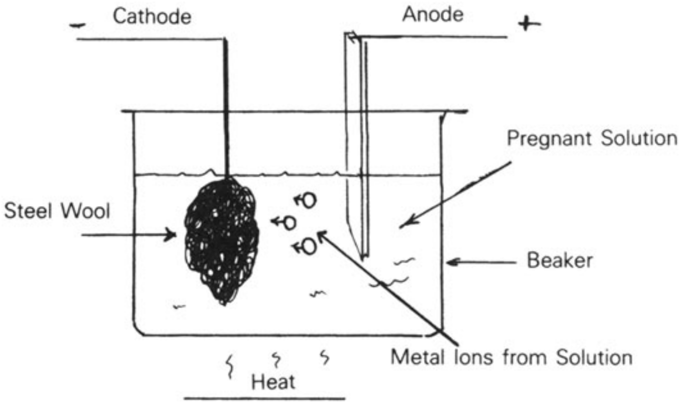


Figure 4.28. Simple steel wool cell for stripping cyanide solutions

it. It is important to use cold water in the diluting process; hot water would decompose the sodium hypochlorite. Wear gloves when handling sodium hypochlorite. It is a strong oxidizer and a fire risk with organics.

If you should accidentally spill a cyanide solution, sprinkle the spill with dry sodium hypochlorite, dilute with cold water, and mop. Always avoid contact, direct or indirect, with cyanide.

Electrical contact points. Electrical contact points are found in such places as relays and switches. Their metallic quality can range from extremely valuable alloys of 25% iridium and 75% platinum, to Mexican silver of an extremely low grade.

Sometimes, knowing exactly where the material came from can provide a clue. An expensive piece of equipment handling high amperage and a large relay or switching cycle raises the likelihood that the points are made of high-quality precious metals, and a little 5-dollar relay should have inexpensive points made of Monel metal or of a thin silver overlay on copper or steel. Sometimes you can be fooled and lose money; other times you can buy cheaply and pick up a sleeper. There is no general advice to offer in this area, except "Be careful."

Chemical medical ware. Here, again, you have to test and assay in order to know what you have and how to part and refine it.

A lot of precious metals and alloys are used in both medical and chemical apparatuses. You will find lab vessels of platinum-clad nickel, platinum-clad copper, and various other base metals that have platinum welded to them in order to protect the vessels' inner surfaces from corrosion without raising their price unnecessarily.

Various basic (alkaline) and acidic solutions. You can purchase or come in contact with all sorts of solutions that might contain valuable metallic ions—stripping solutions, pickling solutions, photographic developing solutions, plating solutions, and so on. Your first step is to identify the solution. Is it acidic or alkaline? Determine this for yourself: Relying on someone else's word as to what a solution is can be dangerous, both physically and economically.

I have made it a policy over the years to only purchase solutions from outside sellers on a percent of the yield basis. If the person with the solution wants the values himself, then I charge him on the basis of my cost to strip and refine the values. To protect yourself, make any agreement very clear as to where you stand.

Many of the tests previously described in this book involved putting the assay into solution, and then testing the solution to identify the dissolved assay. Viewed in this light, if you have a solution that you suspect of carrying metallic values, you are already halfway to an identification.

Most of the identification tests discussed previously used acid solutions, except the one for nickel, which used an acid initially but then called for the solution to be made alkaline with ammonia, after which it was tested with DMG. However, when you begin with an existing solution, you must first establish whether the solution is acidic or alkaline. This is done with pH or litmus paper. Place a few drops of the solution in a small evaporating dish and test it with litmus paper (blue = alkaline, red = acid).

Suppose that the litmus paper is blue, indicating a base. Now, is the solution ammonium or cyanide? Place about ½ in. of the solution in an unheated test tube and hold the tube with your fingers encircling it at the bottom in such a manner that you will be able to detect a temperature change. Hold the test tube under the hood with plenty of draft. See Figure 4.29.

Position your face away from the tube, and, with a bulb or dropper, add four or five drops of hydrochloric acid. In identification testing, always treat an alkaline unknown solution as though it will turn out to be a cyanide solution. Do this

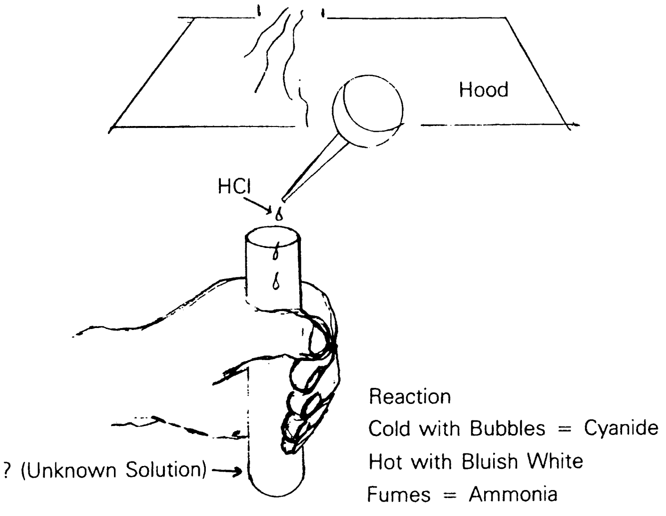


Figure 4.29. Check: ammonia or cyanide?

with great caution. If your solution is cyanide, when the acid is added, the solution will bubble and release gaseous hydrocyanic acid (very toxic), with little or no heat change. If the solution is ammonium, when you add the acid, the solution will rapidly heat up and usually give off white or bluish white fumes (like smoke).

In the case of cyanide solutions, you must make them acidic before you can test them for values. Add a little water to the test tube containing the cyanide solution and boil the solution cautiously. This will decompose the cyanide. Then, add a few more drops of hydrochloric acid. Watch for bubbles; if any appear, you did not boil off all of the cyanide. Check the solution's pH. If it indicates an acid, you are ready to test the solution for values.

Drop a few drops of the (newly acidic) solution into two cavities in the spot plate. In the first spot, drop a crystal of copperas (iron sulphate); if a brown cloud forms, the solution contains gold. In the second spot, add a drop of stannous chloride; if it turns purple to black, the solution contains gold. Remember to check your stannous chloride solution with your gold standard to see if it is still active.

If you drew a blank on gold, take a new sample of 10–20 drops of your original cyanide solution and place it in a small evaporating dish under the hood (with a strong draft). Add nitric acid carefully, drop by drop, until all of the cyanide has been expelled as gaseous hydrocyanic acid, or add three or four volumes of distilled water and boil off the cyanide; then, make the solution in the evaporating dish acidic with nitric acid.

Now, with a dropper, add a few drops of hydrochloric acid to the solution. If silver, lead, or mercury is present, it will come down as a white precipitate. You may remember that the simplest test for determining which metal is in the white precipitate begins with filtering the precipitate onto filter paper and washing it with hot water. You then wash the precipitate off the filter paper into a clean test tube or small evaporating dish and add strong ammonium hydroxide (ammonia). If the white precipitate is silver, it will go into solution; if the solution is then made acidic with nitric acid, it will reappear.

When you are filtering off and then transferring small amounts of a precipitate (as here), the simplest way to make the transfer is to leave the precipitate on the filter paper in the funnel throughout the filtering and washing operations, and then simply to punch a hole n the filter paper and wash the precipitate through the funnel stem into the new vessel. See Figure 4.30.

If your original solution had tested as an acid with litmus paper, the remaining testing would be routine. You would add salt or hydrochloric acid to check for silver chloride precipitation, and add stannous chloride to a spot test to check for gold (purple to black), platinum (deep yellow or brown), and palladium (at first deep yellow, but after sitting a few minutes blue-green). The palladium indication could be confirmed by using a fresh sample in the spot plate and adding DMG test solution to it in place of stannous chloride, producing a palladium precipitate.

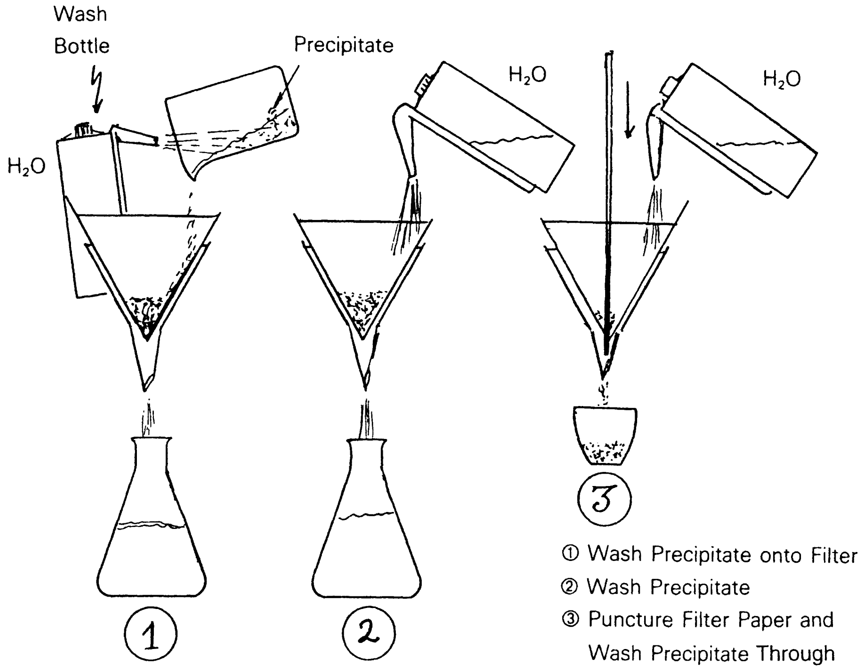


Figure 4.30. Handling small amounts of precipitate

The color of a solution often gives a good indication of what it contains; for example, greens and blue-greens suggest some combination of silver, copper, and nickel.

You could have a large collection of different metallic ions in an acid solution. This would require you to use selective precipitation on the various ions, singly or in groups, to get them out of the solution in order to establish what you have and in what approximate amounts. As I stated in the testing section of this volume, some tests mask your cyanide solution with hydrochloric acid as your first step in testing a cyanide solution, if silver ions had been present, they would have precipitated as silver chloride.

The following metals, in the form of dissociated ions, may be present in an acidic solution (electrolyte): aluminum, antimony, cadmium, chromium, cobalt, copper, gold, indium, iron, nickel, palladium, platinum, rhodium, silver, tin, tungsten, and zinc.

The following metals, in the form of dissociated ions, may be present in an alkaline cyanide solution (electrolyte): cadmium, copper, gold, indium, nickel, silver, and zinc.

You can always drop the metallics out of a solution by adding zinc. This is covered in detail in the chapter on the stock pot.

Do not, whatever you do, mix acid solutions with cyanide solutions.

5

The Platinum Sisters

Platinum and its sister metals, palladium, rhodium, ruthenium, iridium, and osmium, are closely associated. The relationship is so close that you will seldom find platinum alone, unalloyed with one or more of its sister metals.

Platinum is found in gold and silver placer deposits, together with black sands. Platinum and palladium are found and recovered from sulphide ores of nickel and copper, such as the nickel sulphide deposits at Sudbury, Ontario, Canada.

A great portion of platinum-group metals recovered come as by-products of the extraction and refining of other minerals, such as gold, iron, silver, copper, nickel, and cobalt. Platinum and palladium nodules, grains, and flakes are recovered in the classification of black sands. Gold panners often find considerable quantities of platinum alloys as heavy grayish grains in the pan. Another major source of platinum-group metals today is recycled secondary scrap—jewelry, industrial scrap, and electronic and chemical hardware.

In this chapter, I will cover platinum extraction (parting) and refining from scrap, slimes, and muds (such as in a stock pot), from platinum-group alloys, and from free gold separation, panning, and sluicing. As it is unlikely that you will run into a platinum mine as such or a rich deposit of sperrylite ($PtAs_2$), I will not cover platinum extraction from that angle.

Of the six platinum sisters, the ones that are of primary interest to you are platinum, palladium, and iridium. Osmium, ruthenium, and rhodium generally occur in extremely minute quantities; you will probably accumulate so little that you would do far better economically to sell your residues (muds) of these metals to a big precious metals refiner than to try to refine them yourself.

Platinum is insoluble in single acids, in caustic potash or soda, and in cyanide, but it is soluble in aqua regia. It can be compounded as two platinum salts: platinum chloride (the salt of chloroplatinic acid) and platinum diaminodinitrite. Platinum chloride is the more common salt and is the one that is relevant here.

I have described how to inquartate with silver or copper to enable you to make a good separation of gold from those metals by simply dissolving the copper and silver in nitric acid. In that case, the gold was left behind as a powder in a nearly pure state, and the silver was easily recovered as a chloride from the nitric solution, also nearly pure.

Platinum, although insoluble in nitric acid alone, acts strangely when subjected to nitric acid as a component of a silver–platinum alloy. You would expect the silver to go into solution, leaving behind the platinum in metallic form, as nearly pure platinum. Unfortunately, however, if the platinum content of the alloy is 25% or less, the platinum dissolves along with the silver and forms a soluble platinum nitrate compound that is next to impossible to recover as metallic platinum. Even if you have an alloy that is mostly platinum with a little silver, immersion in nitric acid will produce some separation, a lot of residue that is a combination of platinum and silver, and an unknown quantity of platinum nitrate in solution.

In the last chapter, I talked about the problem involved with trying to dissolve green gold in aqua regia caused by silver chloride forming on the metal and covering up the gold. The same problem arises with platinum–silver alloys placed in aqua regia.

Separating Platinum Metals

In this first example, assume you have a mixture of silver, gold, platinum, and gangue, for the most part too finely divided to allow a physical separation and classification.

Cleaning. Spread the material out on a piece of newspaper and pick out the obvious unwanted material—plastic, paper, match sticks. Now, with a horseshoe magnet, work over the material to pick out any magnetics. Go over the material very well. If you keep the magnet inside a plastic sandwich bag, this eliminates the problem of trying to clean the magnet of fine magnetics. Be alert for white gold; some of it is magnetic. See Figure 5.1.

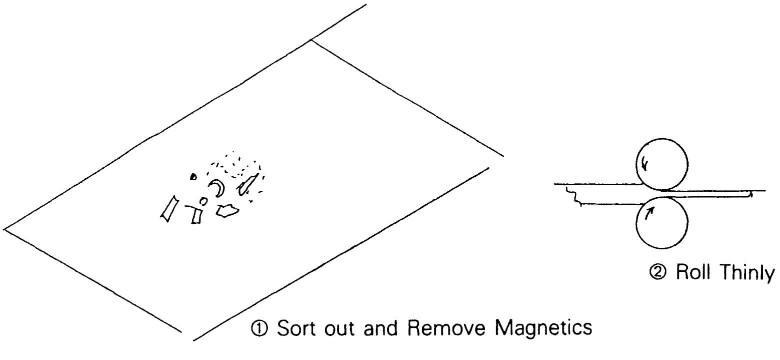


Figure 5.1. First two steps of separation operation

Examine the material carefully for tin/lead solder. If there is any, treat it as is outlined in Chapter 4. If you do not remove all of the solder and wind up with some tin paste, you can get rid of it with a sulphuric acid wash.

Your material could be clean enough at this point, but if there is something such as lint, grease, or shellac in the material, place everything in a casserole dish and boil it well in a strong sodium hydroxide (lye) solution. Pour this off carefully and wash the material several times with hot water to get rid of any traces of lye. The wash water is poured off into a clean plastic bucket. Let it settle overnight and pour it off carefully. Any sediment goes into the stock pot.

If most of the original trash is lint or paper, some operators place the material in a large steel gold pan, pour on some lighter fuel, and set it afire. Drawbacks of this method are that it could set the whole place on fire or that it could melt any plastic you missed and create other problems. Incineration is, nevertheless, a very important step in handling bulk sweeps and bulk hodgepodge electronic scrap.

You can, if you like, put the material into a clean, covered crucible, put the crucible in your furnace, and bring its contents up to a heat just below melting (do not melt). This will burn off most of the unwanted material. I use an electric kiln and simply spread out the material on a clean shelf and bring it up to a red heat (about 100°F), with the kiln door cocked to allow enough oxygen in to convert any carbon present to carbon monoxide (CO). This procedure takes care of plastic, shellac, wax, and oil.

Making thin. Take any thick pieces of material and roll them out as thinly as possible. Place them on a piece of paper, set the rolls close, and run paper and all through (not your fingers). See Figure 5.2. If you do not have any rolls, resort to the hammer and anvil. The material that was rolled or hammered is then heated to a red heat and dropped into cold water to anneal it. Twist the pieces of annealed material so that they will not lie flat in the next step.

Dissolving the gangue. Now place the material in a casserole dish under the hood and cover it with cold aqua regia (one part nitric acid to three parts hydrochloric acid). Do not heat the casserole dish. Platinum is only minimally

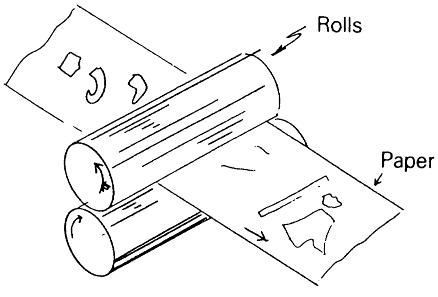


Figure 5.2. Using paper to roll material out thinly

soluble in cold aqua regia, and in this case you want to dissolve as little of it as possible. Your aim is to dissolve everything else away from the platinum.

The gold and silver that are present will go into solution. The silver is at once converted into silver chloride as it dissolves. Some platinum will also go into solution.

At this point, you have an option. You can cover the remaining solid matter with fresh aqua regia, after pouring the spent acid into a large vessel; or you can add new acid to the spent acid. If you choose the latter method, your new acid addition will be diluted by the spent acid and will work slower. Unless you know just how much aqua regia it will take in the first place, it is better to pour off the spent acid and then add fresh.

Acids are expensive and you can waste them if you are not careful. In time, you will be able to gauge pretty accurately how much nitric acid it takes for so much base metal or silver, how much aqua regia for gold or base metal, and so forth. Until you reach this point, though, go slowly and use small batches.

Stirring the material occasionally helps speed up things. If you have a magnetic stirrer, so much the better; put in a spin bar and let it rotate slowly. The time required depends on how much is in the batch, how thin the material is rolled, and how high the temperature is maintained. In this case, you do not want to let much platinum go into solution, so you do not heat the material. The process might take an hour or two or overnight.

Treating the undissolved platinum. When you have dissolved everything that will go into solution, pour the aqua regia off into a large clean vessel (a beaker or glass pitcher). If you have been working with small quantities of aqua regia, pouring them off when spent, and adding new, simply pour the remainder off.

With as little wash water as possible, rinse the platinum off, washing the solution into your collection of spent aqua regia. Examine the platinum. You will find (if there was any free silver, or any gold or platinum alloyed with silver, at the start) that the platinum is covered with a gray-white coating of silver chloride. Wash the platinum off into a cast-iron mortar and grind and pound as much of this silver chloride as you can loose from the platinum; pour this off into the aqua regia solution. Use the wash bottle to chase it out of the mortar. In the spent aqua regia, you have the dissolved gold, a little dissolved platinum, and possibly some dissolved palladium and iridium, along with dissolved base metals such as copper and brass, and free silver chloride.

Add to the aqua regia about 1 fluid ounce of full-strength sulphuric acid for each quart of solution. This will precipitate any lead you might have picked up in the form of lead sulphate ($PbSO_4$). Lead sulphate comes down slowly, so let the solution sit for several hours or overnight.

Final cleaning of the platinum. With the wash bottle, wash the platinum from the mortar off into a clean casserole dish. You will note that the platinum is mixed in with the gray mud (silver chloride) and with whatever silver chloride you did not jar loose with the pestle. If you spot any gold that did not get dissolved, add a little aqua regia to get it into solution, and then wash this aqua regia into your collection.

When you are satisfied that all you have is platinum and silver chloride, add a cup of hot water, stir the platinum around well, and check with pH paper for a neutral indication; then pour this off slowly into the aqua regia vessel. Repeat this until the wash water is clear. The first 2 cups of wash water go into the spent aqua regia vessel; the rest are discarded.

Separating the silver chloride from the platinum. Silver chloride is soluble in ammonia and in cyanide, each with its own separation method.

Ammonia method: Cover the platinum and silver chloride with strong ammonia and stir until all the silver chloride is in solution. Pour this through a filter. Wash the filings onto the filter with a wash bottle containing dilute ammonia water and wash the platinum well on the filter. Remove the filter paper with the platinum on it and set it aside. When dry, the platinum is ready to melt and reuse or sell or refine.

Next, add enough nitric acid to the remaining solution to make it acidic, plus an excess (use your pH papers here); the silver will precipitate as a clean silver chloride, which you can cement as metallic silver, using zinc. If there is very little of the precipitate, you can evaporate most of the remaining ammonia solution and wash the remainder into your stock pot.

Cyanide method: Cover the platinum and silver chloride in the casserole dish with hot water and continue filling the dish until it is nearly full. Check with pH paper for acidity. Add enough sodium hydroxide or lime to bring the water to a pH of at least 11 (alkaline); then add a heaping tablespoon of sodium or potassium cyanide and boil the solution until all the silver chloride is in solution and the platinum is clean. Pour off the cyanide into a clean vessel, wash the platinum with hot water until it is completely free of cyanide, and add these wash waters to the cyanide containing the silver chloride in solution.

Set this aside in a plastic bucket and stir in some mossy zinc or powdered zinc. The zinc will go into solution and precipitate the silver as a metallic silver. Pour off the cyanide, filtering off the last bit and washing the precipitated silver off onto the filter. Wash the silver free of cyanide, then wash it into an evaporating dish and barely cover it with a solution of 1 part sulphuric acid to 15 parts water to dissolve any unused zinc. Pour off and discard this acid solution. Wash the silver free of any acid, dry it, melt it, and sell or re-refine it.

The cyanide system is faster than the ammonia system, but much more dangerous. As I keep repeating, cyanide is a deadly chemical all by itself, and even deadlier in combination with acids. If you have not completely removed all traces of acid before adding cyanide, you can very easily produce deadly hydrocyanic gas. This is the reason for adding lime or sodium hydroxide above and for checking with your pH papers for alkalinity.

Stripping the aqua regia solution of values. In the spent aqua regia solution from your parting operation, there are several values in ionic form, including some platinum and perhaps a bit of iridium. The solution will be a brownish color unless there is considerable copper and nickel as base metals in the batch, in which case it will be green or blue-green.

I have discussed how you must boil the aqua regia down to a syrup-like consistency, add hydrochloric acid, and repeat and repeat until the solution is completely free of nitric acid. Do this under the hood at a medium heat, not letting the liquid evaporate entirely. Then, pour it into a large vessel; wash the evaporating dish with the wash battle and pour this wash water into the thickened solution.

Dilute the solution with three or four volumes of tap water. Let it settle and then pour it off into another large vessel, filtering the last portion to collect any silver or lead salts. The filtrate from this is rejoined to the solution you poured off. Wash the residue on the filter paper into the stock pot and put the filter paper into your filter paper collection container.

The dilute aqua regia solution must be free from any residue or sediment. When it is, you can do a good job of precipitation.

Platinum: The reagent used to precipitate the platinum from the solution is ammonium chloride, which will also bring down any iridium present. However, there is a time delay between the two precipitations, which allows you to catch one and then the other, thereby effecting a separation.

If you are going to sell the values as a platinum–iridium salt or metallic alloy, let them commingle; if not, take advantage of the time element. Use a good grade (CP) of ammonium chloride. If you do not, you will be faced with filtering out the junk to get a clear solution. You need an amount of ammonium chloride that is at least half the weight of the platinum values that are in solution, and preferably an excess. For 1 troy ounce (20 pennyweights) of dissolved platinum, you should use about 12 pennyweights of ammonium chloride. You will need a concentrated solution; try to dissolve as much ammonium chloride as possible in a small quantity of hot distilled water. A good preparation is to make it up as a shelf reagent, at a 4 N concentration, by dissolving 214 g of ammonium chloride (NH_4Cl) in hot distilled water and then diluting the solution to a volume of 1 L.

As is the case with most chemical reactions, heat is a big factor in accelerating this reaction, so you should have your platinum-pregnant solution warm to moderately hot. Pour the ammonium chloride solution into the platinum solution slowly, stirring all the while. When you see a color change (the precipitate—platinum ammonium chloride) taking place, stop. Stir the solution and let it come to rest.

The precipitate usually is bright orange, but this is not always the case: It can vary from orange to bright yellow to an orange– or yellow–maroon. The color is a result of many variables—the concentration of platinum group ions in the solution, the temperature, and the number of contaminants in the solution. A few familiarizing experiments or exercises with pure platinum and mixed platinum metals in advance would become extremely helpful to your analysis at this stage.

The first material precipitated is the platinum. Let this settle. You now have something over an hour before the iridium, if any is present in the solution, begins to precipitate. If you are satisfied with getting a mixture of platinum and iridium, set the vessel containing the platinum aside overnight and let the iridium come down. If you want the two metals separate, you will have to take some steps during the intervening hour.

Iridium: The iridium precipitate that will form is iridium ammonium chloride, a dull green to black metallic salt. As with platinum ammonium chloride, the iridium ammonium chloride's color can vary, but it usually is very dark and always darker than the platinum salt's color.

After the platinum ammonium chloride has settled, siphon off the bulk of the solution into another vessel; then, filter the last portion of the solution onto a filter, adding this solution to the solution that was previously siphoned off. Wash the platinum precipitate down into the point of the filter paper, using a wash bottle filled with a dilute solution of ammonium chloride. The reason for using ammonium chloride solution in the wash bottle is that platinum ammonium chloride is slightly soluble in water but not nearly as soluble in ammonium chloride, and you do not want any of the precipitated platinum to redissolve and run into the solution, which contains ions of iridium, gold, palladium, and so forth.

The solution, now free of the platinum precipitate, is set aside in a cool spot; in time, the iridium will be precipitated. It can be handled in the same fashion as the platinum precipitation was, using the wash bottle filled with the ammonium chloride solution to wash it into the point of the filter. The solution is now stripped of the platinum values and the iridium values.

You could try to get a more complete separation by fusing a platinum–iridium alloy with lead at about 2000°F (or 1000°C), using about eight parts (by weight) of lead to one part of platinum–iridium alloy. Pour the alloy into cold water to granulate, then dissolve the lead with nitric acid. This will leave a residue of platinum and iridium. Wash the residue free of nitric acid and add aqua regia to dissolve the platinum away from the iridium (iridium is insoluble in aqua regia). This leaves the iridium behind as small, bright, nearly pure crystals.

The aqua regia is then stripped of platinum with ammonium chloride, at which point the platinum ammonium chloride will be in a nearly pure state. Of course, you will have to boil the aqua regia down several times with additions of hydrochloric acid to rid it of nitric acid and then dilute the syrupy remainder with three or four volumes of distilled water before attempting to recover the platinum.

You cannot separate the iridium by filtering the spent aqua regia: The solution will destroy the filter paper. Instead, decant the bulk of aqua regia, dilute what remains with distilled water, then filter out the iridium. Add the solution to the aqua regia and the wash liquid from the iridium; then begin your aqua regia boiling operations.

You can, if you choose, when precipitating platinum out of an aqua regia solution, simply let the iridium precipitate on top of the platinum, reduce the orange (platinum) and black (iridium) powder to combined platinum and iridium sponge, and then do a lead fusion separation.

Gold: The gold in the solution can be precipitated as a brown powder by bubbling sulphur dioxide gas through the solution as described in Chapter 4.

Palladium: Your next move should be to recover any palladium that might be in the solution after the removal of the silver as a chloride, the platinum as a chloride, the iridium as a chloride, and the gold as a metallic gold powder.

Unlike platinum, which is only soluble in aqua regia, palladium (the least noble of the platinum group) is soluble in hot nitric acid, boiling sulphuric acid, and fused bases. Because it can be dissolved in nitric acid and sulphuric acid, palladium frequently goes down the drain undetected. If you do your first digestion in nitric acid—to get rid of the bulk of the base metals—before testing for the presence of palladium values, you are sure to lose them.

The palladium is precipitated with sodium chlorate ($NaClO_3$) or potassium chlorate. Sodium chlorate works better but can be dangerous. If it comes into contact with organic materials, it can cause a fire. Do not use any combustible substance in titration to precipitate chlorates.

Put the original solution in a tall glass beaker or casserole dish and bring it to a light boil; then, lower the heat to a point at which the solution is not quite boiling but close to it. Do this very carefully. Put about a teaspoon of sodium chlorate crystals in a large spoon. Place the spoon over the almost boiling solution and shake a few crystals into the solution at a time. The solution will agitate; when it calms down, shake in a few more crystals—carefully, so as not to cause a boil-over. You will need about a teaspoon of the sodium chlorate for every quart of solution, depending on the amount of palladium in solution. The precipitate of palladium is a bright red powder, palladium ammonium chloride.

If the precipitate does not start to form within about 5 min, add an ounce of hydrochloric acid and scratch the inside of the beaker with a glass rod. Scratching its back usually gets the solution going. Avoid interruptions: The palladium ammonium chloride will go back into solution if allowed to sit very long. If this happens, you have to scratch its back again and add some more sodium (or potassium) chlorate.

Use as little chlorate as is necessary to do the job. Practice will help you here. The fumes produced in this reaction are chlorine gas, so work under a good, positive draft. When the solution is stripped, put a few crystals of sodium chlorate on the filter paper and run your red precipitate onto it as well. Wash the precipitate thoroughly and set it aside to dry. See Figure 5.3.

Now spot test the original solution with DMG and stannous chloride testing

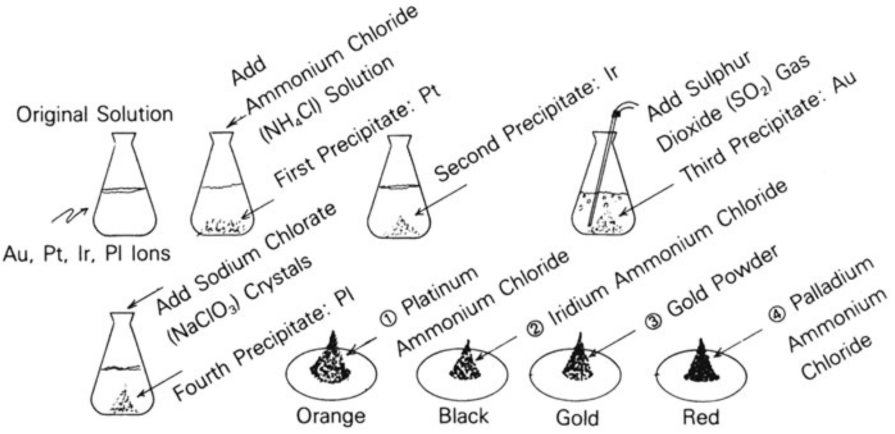


Figure 5.3. Precipitating platinum, iridium, gold, and palladium

solutions. You will probably get a faint platinum indication; it is unusual to accomplish a 100% stripping of platinum values. If you feel that the original solution contains values worth saving, pour it into the stock pot. If not, discard it.

By now, you should have several filter papers holding different precipitates—platinum chloride, palladium chloride, metallic gold, and iridium chloride. The gold powder can simply be melted with a little borax and with a pinch, now and then (during melting), of niter. The metallic chloride precipitates can be heated to drive off the chlorine. This must be done with care. All three chlorides—platinum, iridium, and palladium—are handled the same, and the results of heating them are platinum sponge, iridium sponge, and palladium sponge.

Each precipitate is placed in a glazed evaporating dish on a gas hot plate or over a Bunsen burner and heated just enough to produce white chlorine fumes. If dark fumes appear, the heat is too great and you are driving off values. A good test is to hold the back side of a cool or cold stainless steel spoon over the dish. If a white deposit forms, the level of heat is fine; if the deposit is gray or black, the temperature is too high. See Figure 5.4.

Melting the Sponges

Platinum sponge. Because the melting point of platinum is so high (3190°F), you have to melt it with an oxygen–hydrogen torch or in an induction furnace. Small lots are usually melted with the hydrogen torch in broken-sided crucibles or in special crucibles made for melting small lots, called platinum melting dishes. The oxygen–acetylene torch should never be used for melting precious metals, especially platinum group metals and white gold, because acetylene gas is almost pure carbon. If metallic carbides form, they will make the metal brittle and hard.

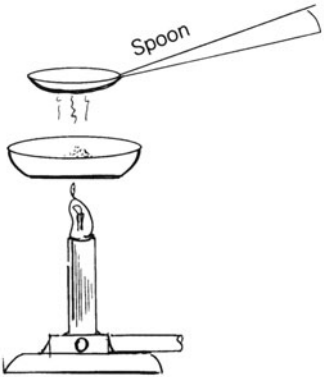


Figure 5.4. Checking reduction fumes from chlorides

Very often, someone will melt platinum with oxygen–acetylene and be puzzled at the sour results. This can also happen with the oxygen–hydrogen torch if you use a reducing flame. Melt the sponge with a slightly oxidizing flame. You must have a pair of cobalt (very dark) melter's goggles, as the light is a dazzling white and is dangerous to your eyes. Place the platinum sponge against the inner back of the crucible. Heat the crucible lightly at first to drive off any moisture in the crucible or sponge.

When the sponge is completely melted into a shiny button, turn off the torch and fish out the button while it is still hot. Place it on the bottom of a crucible, rough side up, and heat to a puddle. Flame polish the rough side (this was the side against the back of the melting crucible). See Figure 5.5.

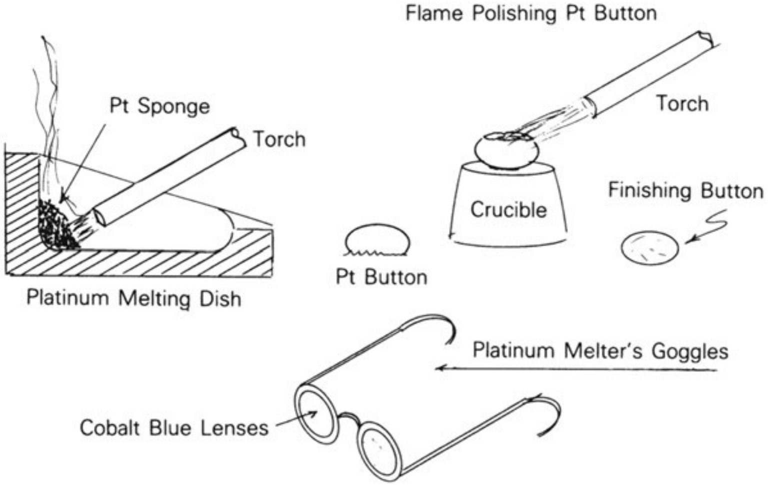


Figure 5.5. Melting platinum sponge

The platinum is then heated very hot and hammered (shaped) on an anvil into a cube, for rolling, if, during the anvil forging, the hot platinum picks up a thin film of iron, this is removed with hot hydrochloric acid.

Platinum is very difficult to cast and is impossible to cast by gravity. Small parts and jewelry findings are cast using the investment casting (lost wax) system on very high-speed vertical spring-driven centrifugal casting machines. Platinum has a sharp, pointed solidification curve. It is, for all practical purposes, solidified in a matter of seconds after the heat is removed.

Iridio-platinum. Iridium sponge and platinum sponge are mixed in the proper percentages and melted together to produce an iridio-platinum alloy that is widely used in both jewelry and the industrial field. A great percentage of the platinum scrap you encounter in secondary refining is iridio-platinum alloy.

Iridium sponge. Iridium melts at 4424°F (2442°C). It is difficult to melt and impossible to work cold. Its melting point is too close to the maximum temperature of the oxygen–hydrogen torch for that tool to be useful. You can melt it with an oxygen–acetylene torch if you are very careful with the torch adjustment, or with an electric induction furnace. Your best bet is to sell the iridium as an iridium chloride or sponge.

Palladium sponge. Palladium has a melting point of 2822°F (1554°C). Melt in a slightly oxidizing flame. When the metal is completely melted, rather than simply removing the torch, slowly reduce the oxygen to the torch as you back the torch off. This will allow the palladium to solidify while being subjected to a reducing flame. Palladium has the ability to absorb great amounts of oxygen when molten; if it is not allowed to solidify in a reducing atmosphere, the molten palladium will swell from the occluded oxygen, leaving you a rough, useless button. If this should happen, remelt just the top of the button and let it solidify under the reducing flame until you get a satisfactory button.

If the edges split while the button is being rolled, this is a sign of occluded gas problems during solidification. Palladium should be rolled while the button is hot. The operation of flame polishing or remelt is called "sweating" the button. This reaction is similar to the spitting of silver when melted: Pure silver also absorbs oxygen when molten, and when it goes from a liquid to a solid, it will spit (give off its oxygen).

By now it is evident that the method of extraction (separation or parting) used for a particular metal is dependent on the identity and characteristics of the other metals (and other elements) present in the original material. Generally, the more metals there are in the original material, the more complex the task of separating the values individually and without waste becomes.

The key to understanding selective precipitation is knowing what is soluble in what solvent and what will precipitate from what solvent, given the appropriate chemical addition. It is also extremely important to know the different behavior that metals will exhibit in acidic and basic solutions.

The purifying (refining) stage is usually just a repetition of the original process several times over. Each time through, you accomplish a closer or more perfect separation, resulting in a finer end product.

Always use high-grade brand-name equipment. You will also be safer and better off to use larger equipment than necessary. If you have 1 quart of liquid to evaporate or process, use a 2-quart container; in other words, give yourself lots of room.

Platinum

Platinum is a tough bird to put into an extractive solution or gas-phase extraction. However, if tackled correctly, going with a low-tech course of action, it is not all that tough to extract or separate platinum from ore bodies, mixed scrap or auto cat converters, and so forth.

Why So?

A great many extractive methods are overly complicated due to many reasons:

1. Whether the person chasing the platinum (Pt) has a clear understanding of the Pt electron populations and how they are distributed around the nucleus.
2. Extractive processes seem to operate on momentum. A complicated extractive system will survive generation after generation simply because that is the way to do it.
3. Chemistry, regardless of whether it is organic or inorganic is broken down into chemical systems. Each of these systems has various laws which govern what it will do under various conditions that exist or are made to exist. There are various laws between systems. Unless you understand these laws (rules), you are reduced to 40,000 dixie cups to try to affect a solution.

Platinum—Pt

Platinum is an element belonging to the triad osmium, iridium, platinum. The three, Os, Ir, and Pt, are referred to as a triad group because of the remarkable similarities among the three. Lets look at the electron shells of all three.

Osmium Shells	K	L	M	N	O	P
Number of electrons in each shell	2	8	18	32	13	2

Iridium Shells	K	L	M	N	O	P
Number of electrons in each shell	2	8	18	32	15	2

Platinum Shells	K	L	M	N	O	P
Number of electrons in each shell	2	8	18	32	17	1

Osmium, iridium, and platinum are known as the heavy platinum metal triads. Palladium, rhodium, and ruthenium are known as the light platinum metal triads.

All six metals are all very nonreactive, and their compounds are generally so unstable that on being heated, the compound decomposes to give free metal. As a result of this instability, they occur in nature as free metal. The exception is the mineral sperrylite (PtS_2). Due to the atomic similarity of the two triads, they are commonly found occurring together in the form of binary, ternary, and quaternary alloys.

The other closely related triad consists of iron, cobalt, and nickel. Therefore, the group-VII elements consists of nine metals forming three triads.

Iron	Ruthenium	Osmium
Cobalt	Rhodium	Iridium
Nickel	Palladium	Platinum

The close relationship is the reason a considerable amount of platinum metals are recovered from the nickel smelting operation in Sudberry, Canada.

Looking at this group of triads, it becomes very apparent by their electron population in the various shells that they are very closely related.

Platinum's Monograph

Atomic weight = 195.23
Atomic diameter = 2.769Å
Mass number = 195
Density at 20°C = 21.37
Hardness = 4.5
Melting point = 1773°C
Boiling Point = 3827 ± 100°C
Å (ångstrom) = 10^{-10} meter (39.3701 in.)
1 Å = 0.00000000393701 in. long

Orbital Distribution of Electrons in Various Energy Levels

K shell: 2
L shell: 2 in the "S" subshell, 6 in the "P" subshell
M shell: 2 in the "S" subshell, 6 in the "P" subshell, 10 in the "D" subshell
N shell: 2 in the "S" subshell, 10 in the "D" subshell, 14 in the "F" subshell
O shell: 2 in the "S" subshell, 6 in the "P" subshell, 9 in the "D" subshell
P shell: 1 in the "S" subshell

The electron population and its distribution just given is usually where the electrons live at ground state at ambient temperature.

Crystal structure of Pt is cubic-face-centered.

Its first ionization potential is 9.0 (eV); its oxide would be basic.

Platinum's solidification range is very short. It is really like a sharp peak. The solidification range is the range of temperature over which it is liquid. This short solidification range makes it virtually impossible to gravity cast platinum. It is either liquid or solid and this short temperature range between the two states is the problem. You can make some small platinum castings by centrifugal casting the metal into investment molds with a real fast, spring-actuated special casting machine called a "troit." Try as you may, you can melt platinum in a melting dish with a hydrogen torch, but you cannot pour it out as a liquid stream. The moment you remove the torch, the liquid platinum becomes solid.

Outside of centrifugally cast jewelry items, dental castings, and small items, most platinum items are produced via forging, drawing, stamping, and so forth. Gray iron is called cast iron because of its ease in gravity casting. This is due to its solidification range. The ability to remain very liquid over a wide temperature band.

Understanding Atomic Structure

As with any method of precious metal recovery and refining process, it is necessary to have a fair understanding of the atomic structure of the particular element you are chasing. By this, I do not mean you have to be a Ph.D. in inorganic and organic chemistry. The key is actually rather simple. You have to look closely at the valence electrons and determine how you can get one or more to combine with some other element to form a molecule which is soluble and can be broken apart in order to separate off the metallic element you wish.

Before I get into the platinum atom, let us clear up exactly what is meant by valence electrons and how they operate.

Valence

Let us take a much simpler element to look into valence and what is called ionic bonding. A good example of a simple element is sodium. Sodium is a silvery white, extremely soft metal which can be cut with a dull knife, like cheese. Let us look at a sodium atom presented in Figure 5.6. The nucleus as we see is in the center of the atom; in this case of an atom of sodium, it contains 11 electrons and 11 protons in a very small tightly packed bunch.

A proton consists of a subatomic particle with a positive + equal in magnitude to that of an electron. In other words the electrical charge on a proton is positive and of the same strength as the negative charge on the electron –, thereby they cancel out each other electrically. Protons and electrons have the same electric charge but are of opposite sign.

The electronic charge is the negative electric charge of the electron (1.6021×10^{-19} coulombs (C), therefore the positive charge on the proton is a positive electric charge of 1.6021×10^{-19} C, or 0.00000000000000000016021 C; really not much electrostatic energy.

To clarify this, as we are more used to dealing in amperes and much larger units, let us look at 1 coulomb. The quantity of electricity transferred by 1 ampere in 1 second is one coulomb. So we are looking at very small packets of electrostatic energy.

In the nucleus we also have 11 neutrons. A neutron is also a subatomic particle, having no charge; it is completely neutral. Its mass is approximately 1.675×10^{-24} g or 0.000000000000000000000001675 g each. It has about the same mass as a proton which has a mass of 1.672×10^{-24} g each. It is slightly heavier than the proton.

You see the word isotope; platinum isotopes, gold isotopes, and so forth. These

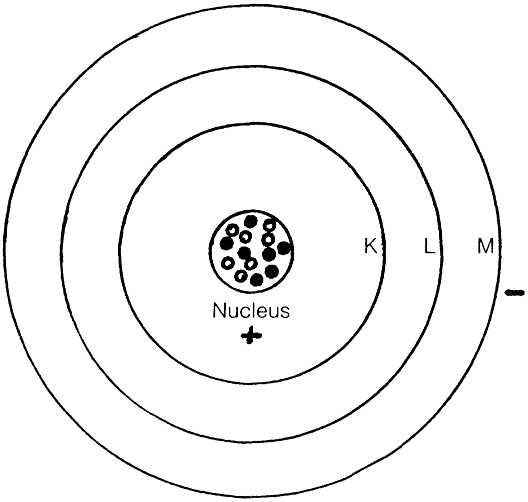


Figure 5.6. Graphic view of a sodium atom

are simply atoms of gold or platinum or whatever atom that contains one or more extra neutrons in its nucleus than are protons in the nucleus. Some isotopes are stable and some are unstable. There are seven platinum isotopes.

Shells + Electrons

We really do not have any concern about the nucleus of the atom. Our main concern is the electrons and their locations in various shells. We can do something about these electrons, at least some of them, in order to accomplish our goal, which is the separation of platinum from whatever gangue, another metal, a solution, or what have you to isolate it.

In fact, we are not really concerned with all the electrons in the various shells and subshells but only the valence electrons. These are the ones which enter into chemical reactions. Most periodic tables do not list the entire electron population and the shell and subshells in which they are located; but they only show in what shell and subshells the valence electrons are located.

Platinum: $4f^{14}\ 5d^{3}\ 6s^{1}$
Sodium: $3s^{1}$
Chlorine: $3s^{2}p^{5}$

Shell	
K	first shell, 1 subshell *spdf*
L	second shell, 2 subshells *spdf*
M	third shell, 3 subshells *spdf*
N	fourth shell, 4 subshells *spdf*
O	fifth shell, 5 subshells *spdf*
P	sixth shell, 6 subshells *spdf*

In other words, platinum has 14 electrons in the N or fourth shell and they are in the *f* subshell, 3 electrons in the O or fifth shell and they are in the *d* subshell, 1 electron in the P or sixth shell and it is in the *s* subshell, for a total of 18 valence electrons. We are not concerned with the electrons in the K, L, and M shells.

Do not despair now, stay with me, things will start to get clearer and clearer as I get into the actual "do it" phase. When we get further down the line, you will see how even the most basic understanding of atoms, bonds, and so forth, makes it much easier to actually capture platinum.

Electrons

Back to the electrons and our sodium atom. The reasons I chose sodium is its simplicity and its huge role in the recovery of many, many metals.

The electrons of the sodium occupy various shells which extend out beyond the nucleus in a definite arrangement. The 11 electrons, 11 protons, and 11 neutrons and their arrangement are what makes sodium, and sodium only, not lead or any other element; just as platinum is platinum due to its make up and arrangement of 78 protons, 78 neutrons, and 78 electrons. We see that the 11 electrons orbiting around the nucleus occupy shells K, L, and M: 2 electrons in the K shell, 8 electrons in the L shell, and 1 electron in the M shell. There is nothing in the N, O, P, and Q shells. So when we talk about the electron shells of sodium, we simply forget N, O, P, and Q shells.

The seven shells (K, L, M, N, O, P, and Q) are all we need to cover all the elements that we are aware of today. Who knows when someone will find a new element requiring an R shell?

The magic number for the outer shell is 8. The atoms of all elements have 1 electron in the K shell and 8 electrons in the L shell, except hydrogen, helium, lithium, beryllium, boron, carbon, nitrogen, oxygen, and fluorine. All atoms have 2 electrons in the K shell except hydrogen which has 1 electron.

What we are interested in is what is called the valence electrons. Those electrons which are in the M, N, O, P, and Q shells are the only electrons that can enter into a chemical reaction. With the exception of hydrogen and helium in which the K shell is its valence shell, and with hydrogen, helium, lithium, beryllium, boron, carbon, nitrogen, oxygen, fluorine, the L shell is their valence shell. Now to the magic number of 8 electrons in an atom's outermost valence shell.

Ionic bond

All atoms are trying to fill their outermost valence shell. When this happens they become extremely stable. In order to do this, they (atoms) will share or donate electrons. This is called bonding, which is a chemical bond.

Valence

Elements are listed as having a positive valence or a negative valence. Let us clear this up. When we state that an element has a + valence of 1, we are not referring to a plus electrical charge. In this case, we are referring to the fact that this particular element has 1 electron which it can donate to a chemical reaction with another element that can accept an electron. If an element has a minus valence of 1, it indicates that it can accept an electron to a chemical reaction, not a negative charge.

We are talking numbers, not electric charge of plus or minus. Looking back at our sodium atom we see it has 1 electron in its most outer shell, which means it can and will (under the correct conditions) donate that electron to an element which has a spot to put it or is short an electron.

Now, let us look at a chlorine atom; see Figure 5.7. In the valence shell of chlorine we have 7 electrons. (Note: Most metals have a + valence and nonmetals have a – valence) which would indicate that it has a – 1 valence. So, if we can get the sodium atom to donate its excess baggage of 1 electron to help out the

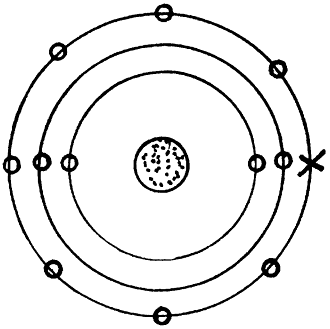


Figure 5.7. Chlorine atom electron arrangement

chlorine fill its outer shell with the magic number of 8, as it has 7 already, then both the sodium is happy and the chlorine is happy, and we now have a whole new ball game. We do not have sodium metal nor chlorine gas, but table salt. What we have here is an ionic bond or a transfer of electrons.

We have what is called a metallic salt. Now, if we take the compound which we now have consisting of 1 atom of sodium, a metal, and 1 atom of chlorine, a gas, we can dissolve this salt in water, separating the sodium from the chlorine freely swimming around in water (H_2O), but when we did this, the sodium did not get back its donated valence electron, and as the chlorine did not give up the electron it borrowed from the sodium to fill its outer valence shell, we now have free roaming ± sodium ions and – chlorine ions.

Now we are talking electrical charge. With our sodium ion we are missing 1 electron with a minus electrical charge, therefore we now have 11 positive protons in the nucleus and only 10 negative electrons in the shells. Therefore, we are out of balance electrically, so to speak, by having one more + than –. The sodium ion is more plus electrically by one, so it is sodium + and is called a cation, and our chlorine ion has an extra electron against nucleus protons, so we have 17 protons + and 18 electrons –. It becomes more negative than positive by 1 electron and is called a –1, a chlorine anion.

Of course, if we evaporate off the water, the salt will reform as sodium chloride.

Now, we have been talking about atoms: 1 atom of sodium, 1 atom of chlorine. A single salt crystal is made up of a lattice work of a huge volume of atoms of chlorine and sodium; in this stage, 1-to-1. Let us not get off of the track. NOTE: An ionic bond is a bond between atoms where one or more electrons are transferred from one valence shell to another. A covalent bond results in the sharing of electrons.

Reactions

Any reaction in which an atom loses or donates electrons is called oxidation. In our case, when the metallic sodium loses its 1 electron to the chlorine, it is in its first oxidation state, sodium +.

In the case of the sodium, you have oxidized it as far as you can go, as the next shell down is full up with 8 electrons; there is no place to get any more electrons. It is happy and has nothing more to donate to a chemical reaction or bonding. It can only go one way and that could be to get its lost electron back from the chlorine and become sodium metal again. The chlorine ion now having completed its outer valence shell with the electron it took from the sodium is in the same boat with the sodium. Both have a full outer shell of 8 and are happy.

Hydrolysis

Dissolving a substance, in our case sodium chloride (salt) in water as in Figure 5.8 is known as hydrolysis. It is accomplished due to the fact that the water molecule is a polar molecule and will pick the salt apart electrically, so to speak.

Reversing the Process

It is a separation game anyway you look at it. What we are after is to get what we want to recover or separate from something else. In some cases, we must do some conversion of the material we are trying to extract in order to get it to separate from gangue and so on.

Separations

If we have very finely divided platinum, gold, copper, and so on distributed among gangue material and it is impossible to separate them with any degree of success mechanically, we get it to couple up with another element which will produce a soluble salt molecule of which the value we want is part of that molecule. We must separate the constituents of the salt back into the elements that made up the salt molecule. This is the basis of all leaching, cyanide, thiourea, acids, and so forth, even gas-phase extraction.

Let us continue with our example of salt (NaCl). Let us say that we have a salt mine and we wish to extract the sodium as a metal and the chlorine as a

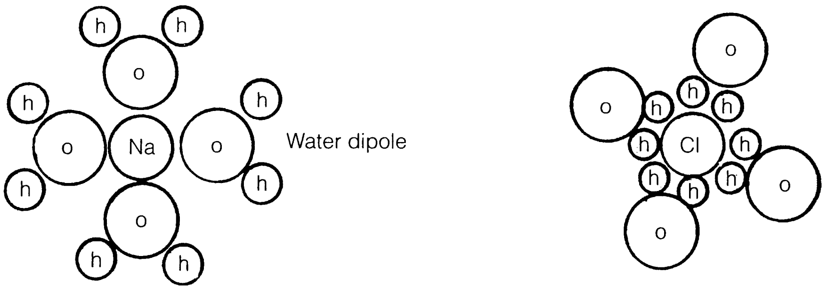


Figure 5.8. Disassociated chlorine and sodium atoms in water

gas, or we just wanted the chlorine. Now remember, once we have dissolved the salt in water to a soup of free roaming cations and anions, each with a full 8 electrons in their outer shell surrounded by a water dipole (molecule of water), we have a problem. If we evaporate the water as I have stated, we end up again with NaCl.

Because they are both full and happy, the chloride is in no way going to send over the electron it borrowed from the sodium of its own free will. The sodium is really not interested anymore. The only thing either will do for each other is to share the lone electron; however, the water dipole prevents the rearrangement. Let us look at a neon atom; see Figure 5.9.

The neon atom next to the sodium cation and the chloride anion—all three have a full outer shell of 8 electrons. So all three are unable to take part in a chemical reaction, as they have no valence electrons which they can donate or accept, nor do they have any spots open whereby they can accept 1 or more electrons to form a molecule.

The big difference between the neon and our sodium cation and chlorine anion is obvious. Our neon is at ground-state 0 electrical charge as it has 10 protons + charge in its nucleus and 10 electrons – charge in its shells, 10+ and 10– equals 0; now with 8 electrons in its outer shell, its all locked up—nothing to donate nothing to accept. So what we have is an inert gas that will not play ball at all, no such thing as CuNe, AgNe, AuNe, one of a family of noble gases helium, neon, argon, krypton, xenon, and radon. Radon has been in the news quite a bit lately because it is radioactive. Now, the big difference with our sodium cation and our neon atom is that our sodium cation is really a neon atom now, or is it? It is the same except for the fact it has 11 protons + and 10 electrons –. So it would look like a neon atom with a +1 electron charge.

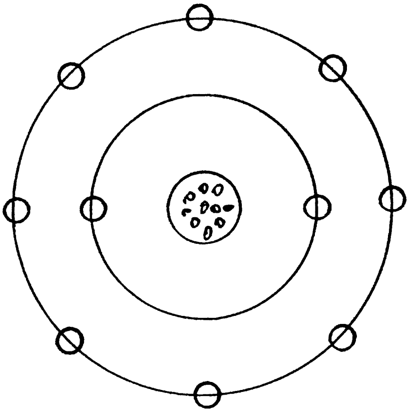


Figure 5.9. Action of dissolving NaCl in water; dipole action of HOH

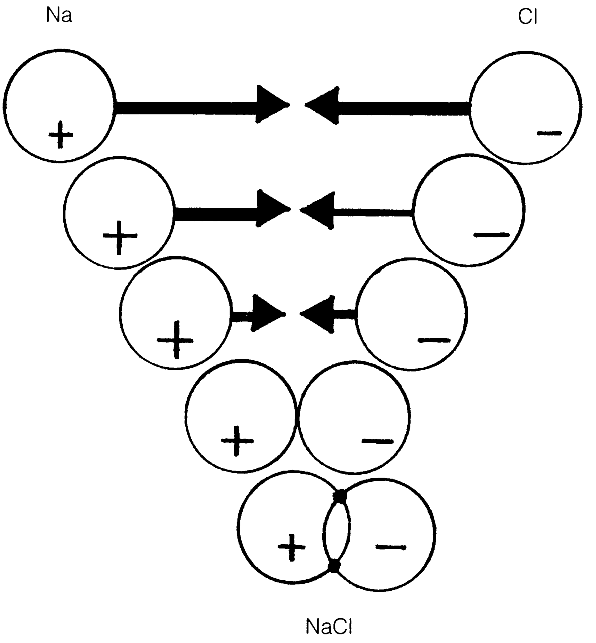


Figure 5.10. Sodium and chlorine recrystallization as water is removed by evaporation

As we have covered this, we know that in a water solution of NaCl we have + sodium cations and – chlorine anions which cannot get back together to form the NaCl molecule due to the polar nature of water. Unless we drive off the water, the unlike electrical charges will attract each other and the sodium + and chlorine – get back together; see Figure 5.10.

Outside Help

So how are we going to get back if we choose Cl° gas and Na° metal. As we know, we can separate Cl^- and Na^+ in solution. The answer to this is simple. We have in solution, sodium cations each with a + charge and chlorine anions each with a – charge, so all we have to do is somehow bring in some + and – electric charges from outside of the system so we can add a – to our sodium cation to give us Na° in place of Na^{+1} and we are back to metallic sodium and snatch away a – electrical charge from our clorine anion Cl^{-1}, bringing it back into Cl° gas. What we do is set up a DC electrical source and an anode and cathode, and as we know, + and – charges attract each other if our outside charge is strong enough to overcome the water dipole's grip on both the anions and cations and their mutual + – attraction to each other. What will happen is shown in Figure 5.11.

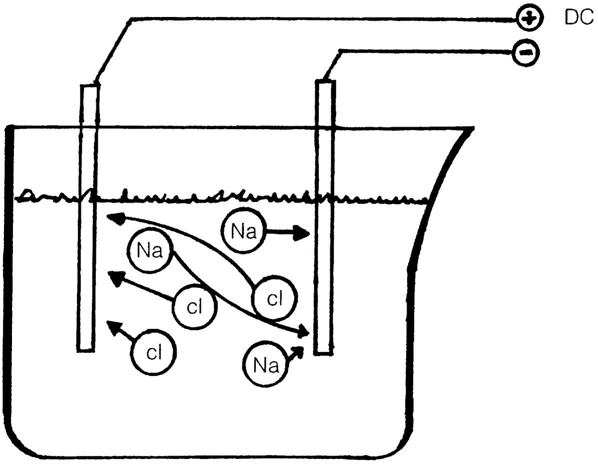


Figure 5.11. Direction of movement of sodium and chlorine in solution when a DC charge is applied

Plating

Plating is the basis of all electroplating, electrowinning, and electrorefining. Actually we would not recover metallic sodium at the cathode due to the fact that the instant the sodium cation picks up its lost negative charge and becomes Na° (sodium metal), the water present would in the matter of a nanosecond convert the metallic sodium to NaOH (sodium hydroxide, lye). In fact, this is how NaOH is produced from salt brines.

You would, however, produce Cl_2 gas chlorine at the anode where it lost its extra negative charge. Chlorine is always abbreviated as Cl_2 as it is diatomic—that is, two atoms of chlorine coupled together for stability to form a molecule of chlorine. Oxygen and hydrogen are also diatomic and are written as H_2 and O_2: 2 hydrogen atoms equal 1 hydrogen molecule; 2 oxygen atoms equal 1 oxygen molecule. So when you say that you have a molecule of water, this would be incorrect. What you actually have is 2 H_2O or two molecules of water.

Chlorine gas ↑ Sodium → (Metal)

Should we simply melt the salt to a liquid, we could and would produce both metallic sodium at the cathode and chlorine at the anode. This is done in a special molten salt plating device called a Downs cell.

You will note that the sodium metal which is reduced at the cathode floats due to its specific gravity of 0.971, which makes it quite light for a metal.

In summary, to separate a molecule of salt into sodium cations and chlorine anions we have to pull it apart with water dipoles, which is easy as the water molecule is – – on one end and + + on the other end as shown in Fig. 5.8.

If we back to the + + end of the water dipole to a −1 chlorine anion, and the − − end of the water dipole up to the + sodium cation, we have a 2-to-1 tug of war, and as the sodium chloride molecule is held together by only a 1+ and 1− electron attraction, it is no contest.

We now know why some salts will dissolve using water as a solvent. The water dipole molecules simply pull the salts apart electrically.

Rust

Let us take a crystal lattice of iron (a huge collection of iron atoms) that is enough to make up a piece of iron we can handle and see. Can we pick the iron apart with water dipoles? Reduce it to rust (iron oxide)? Not really. The oxygen in the air will form an oxide film over the iron. The film, if not toothed or cracked, is actually good, as it makes the iron passive to further rusting.

What does this have to do with platinum? Bear with me and you will see. Now, if this iron becomes wet (for example, rain) and the passive coat of Fe^{2+} is so thin as to be porous or cracked, the H_2O gets between the rust Fe^{2+} and the fresh unoxidized iron below. The layer of Fe^{2+} on top of iron + + cations enter into the aqueous solution H_2O covering Fe°. You have created a mini electroplating cell by the following reaction:

$$Fe^{2+} + 2OH^- + Fe(OH)_2(O) \rightarrow Fe_2O_3$$

making more rust. This is sometimes called a corrosion cell. A piece of iron 1 in. thick will produce 8 in. of rust.

This is the common brown iron oxide with which we are all familiar: ferrous hydroxide [$Fe^{2+}(OH)_2$ and ferric hydroxide [$Fe^{3+}(OH)_3$]. Although it is not a true oxide, it is, however, referred to as rust or iron oxide.

Ferric—Ferrous

I intend to harp a little more on this game of donating electrons and accepting electrons, valence electrons. As you understand this, how and why it works, you then will be armed with the key to any chemical extraction of most any metal or nonmetal you wish.

In our look at sodium chloride, the sodium donated 1 electron to chlorine which could accept only 1, leaving both with 8 or filled outermost valence shells like neon, so nothing else could happen. Remember, 8 electrons in the outermost valence shell is kings X. You have Na^+Cl^- and that is it; no Na_2Cl or $NaCl_2$. This would be impossible. Two sodium atoms both with a valence of +1 cannot couple up with a chlorine atom with a −1 valence because there is only room for 1 electron to fill in to add to 8 Na_2Cl. The opposite you could not couple up (form a molecule) consisting of $NaCl_2$, one sodium atom and two chlorine atoms.

Remember chlorine is a molecule of two chlorine atoms Cl_2, as you have in a molecule of salt 2NaCl. Remember H_2O is actually $2H_2O$.

In our discussion about rust, I show two iron compounds (molecules). One is called ferrous hydroxide [$Fe^{2+}(OH)_2$ or $Fe^{2+} + 2\ OH^-$, and the other is called ferric hydroxide [$Fe^{3+}(OH)_3$ or $Fe^{3+}2OH^{2-}$].

Now you have "ous" and "ic." Let us pick formulas apart. Let us take ferrous hydroxide [$Fe^{2+} + (OH)_2$] first. Fe is the abbreviation for iron. The 2+ means that the atom has an electrical charge of plus 2, as 2 electrons in the outer valence shell have been donated to the reaction $Fe^{2+} + 2OH^-$ to make ferrous oxide. The $2OH^-$ means two hydroxide molecules, both of which accepted one each of the two electrons donated by the one iron atom which makes them more negative by 2 electrons as a pair, making it balance.

Now what is OH usually written as? OH is called a hydroxide radical. Now let us define both hydroxide and radical. NOTE: Lye is caustic soda or sodium hydroxide (NaOH), a sodium atom + 1 hydroxide radical. Now, remember that our sodium had a +1 valence and only 1 electron it could donate to a chemical reaction, as the next shell down had 8. From this, you could assume correctly that in the molecule NaOH, the OH has to have a valence of −1. Like chlorine, there is only one slot to fill.

Hydroxide: An hydroxide is simply a compound derived from water (H_2O). This comes about by replacing one of the hydrogen atoms of water with some other atoms, such as NaOH (sodium hydroxide). Metallic sodium is $Na^\circ + H_2O = Na^{+1} = OH^{-1}H$ (g). The one hydrogen atom lost or replaced by the reaction between sodium and water goes off as a gas.

Radical: A radical is a group of atoms present in a series of compounds, which maintains its identity. A radical is usually incapable of independent existence: the ammonium radical (NH4–), the ethyl group (C_2H_6–), and, of course, the hydroxal radical (OH–). A free radical is a radical that may exist independently for a short period. The radical, of which we have two in our formula, is usually written $2\ [OH]^-$. The boxing in simply indicates that the two act as a single entity.

In Figure 5.12, we see the basic orbital distribution of electrons in the various shells. In the valence shells, we have 14 in the M shell and 2 in the N shell. Iron has a valence of +2 or +3 which, as we now know, means it has and can donate 2 or 3 electrons to a chemical reaction (that is, $FeCl_2$ and $FeCl_3$). In ferrous chloride, the iron atom lost or donated 2 electrons, 1 each to 2 chlorine atoms = ("ous"); in $FeCl_3$ the iron atom lost or donated 3 electrons, 1 each to 3 chlorine atoms = "ic." It is a new game.

There is an old saying that if you have an elephant to eat, you do not walk up and bite him; you must cut him up into bite-sized chunks first. Our elephant, in this case, is platinum.

So we look at some easier things to cut up and eat before we tackle platinum. We practice, so to speak.

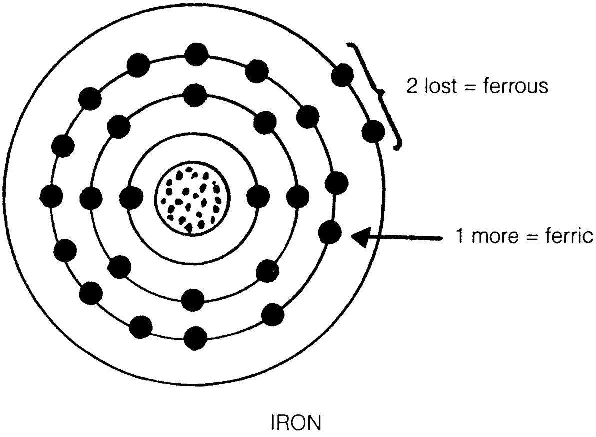


Figure 5.12. Electron arrangement of an atom of iron

Subshells

Removing 2 electrons from the N shell gives us ferrous, then further oxidizing by removing 1 electron from the M shell gives us ferric (Fe^{3+}). Figure 5.12 shows 14 electrons in the M shell when the iron is ferrous (Fe^{3+}). Looking at this diagram, one would suspect it would be much harder to capture an electron from a shell with 14 going for it, then to capture the first 2 electrons from the outermost shell. Well, if you assumed this, you are correct. However, the atomic structure shown is very general and it is a bit more complex.

The reason I am going into this is because when you set out to extract any metal, precious or nonprecious, an understanding is needed of the orbital distribution of the electrons in various energy levels (shells) and what it takes in the way of energy to remove 1 or more electrons from the atoms of an element in order that it will enter into a chemical reaction.

The electron shells L, M, N, O, P, and Q are subdivided into subshells *s, p, d,* and *f.*

As we have already discussed, the valence electrons in N, O, P, and Q is what we are interested in, and whether an atom has a plus valence (electrons it can donate) or a minus valence than an atom that can accept (spots to fill in).

What we can or cannot accomplish as far as a chemical reaction, bonding, forming molecules, and so forth depends on the orbital distribution of electrons in various shells and subshells.

Now let us look again at the iron atom, but this time, let us look at the actual distribution of electrons at ground state. Ground state is defined as the most stable energy state of an atom or molecule. In our case, we are talking about the normal state of an atom when its electrons move in orbits such that the energy of the atom is a minimum (calm and unexcited).

Energy Required

It takes energy to put platinum, gold, copper, and so forth into a soluble metallic salt (for example, gold chloride and platinum chloride), and in order to do this, we have to get the atoms of the element to donate one or more valence electrons to something with a – valence to form a molecule of metallic salt [that is, NaCl (sodium chloride), AuCl, $AuCl_3$, Pt^+ (gas), $Pt(OH)_2$, PtCl, $PtCl_2$]. This takes energy. This energy that is required is called electron volts and the amount required is called ionization potential.

I have already defined the electron volt (1.602×10^{-19} C = 1 eV). Now, let us look at the energy to ionize a platinum atom (remove electrons), making the atom a cation, Pt^+ (cation.)

Let us talk about the ionization potential of platinum. The ionization potential is the amount of energy in electron volts (eV) that it takes to remove an electron from an atom, making it a cation (positive charged ion). In most cases, we are interested in just removing 1 electron from the outermost subshell. This is called the first ionization potential. In this case of platinum, this potential is 9.0 eV. See Figure 5.13.

If we remove the outermost electron from the platinum atom it is going to take 9 eV of energy to do so. Also, it takes 9.2 eV to remove the outermost electron from a gold atom. Here we have a paradox. We all know it is harder to dissolve Pt than Au, so how come it takes more energy to convert a gold atom to a gold cation. $Au^\circ + 9.2 \text{ eV} = Au^+$ cation, $Pt^\circ + 9 \text{ eV} = Pt^+$ cation. One only

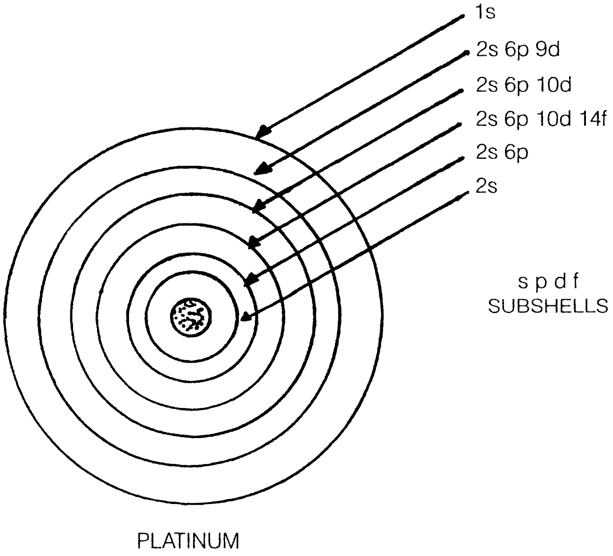


Figure 5.13. Electron arrangement of an atom of platinum

knows that if you put a 1-g piece of platinum wire in aqua regia along with a 1-g piece of gold in the same solution side by side, the gold is dissolved in no time and has been converted into soluble gold chloride and the gold is in solution; the platinum simply sits there, virtually unaffected.

It is only after extensive boiling at high temperature in strong aqua regia that we can dissolve the platinum wire. In fact, it is almost impossible to dissolve a large hunk of platinum (say weighing ½ troy ounce) in aqua regia. It can be done, but it is going to take a lot of time, aqua regia, and heat.

In fact, although both platinum and gold are soluble in aqua regia, the best method of separating a mixture of small particles of platinum and gold is to place them in cold aqua regia until the gold is in solution, the filter off the platinum and precipitate the gold from the filter solution. (This will be covered later).

The reason that Pt is harder to dissolve than Au lies in its specific gravity (SG) or density. Gold has a SG of 19.32 and platinum has a SG of 21.37; therefore, it is in the packaging. A 1-ounce package (hunk) of platinum is much smaller than a 1-ounce package (hunk) of gold. If we were to think of angstroms (1 angstrom = 1 meter × 10^{-10} which is 0.0000000001 meter long which is quite small).

In a dimension with which we are all familiar, say 1 in. = 1 Å, then a gold atom would have a diameter of 2.878 in. and a platinum atom would have a diameter of 1.769 in. This difference, as small as it seems, makes it possible to "cram" a lot more platinum atoms into a given area than gold atoms. This tighter packaging makes it much tougher to pick away at individual atoms, getting them to donate 1 or more electrons to a chemical reaction.

Tougher Picking

As you pick off electrons further down toward the nucleus, the job becomes tougher and tougher. With platinum, it gets real tough. To go from Pt° to Pt^{+}, the first oxidation state takes 9 eV of energy. Now, to go from Pt^{+} to Pt^{2+} to Pt^{3+}, 23.6 eV are needed, and from Pt^{3+} to Pt^{4+}, you are looking at 41.1 eV; at Pt^{5+}, you are out of business, so to speak. Let us pursue this a bit further.

Electronegativity

There is a factor called the electronegativity of an element. This is simply the power of an atom in a molecule to attract electrons to itself. Now, as a metal, in the chemical sense, is an electropositive element (one which loses electrons readily in a chemical reaction), it becomes positive electrically by the number of electrons donated to the reaction (that is, Pt^{+} takes 1 eV, and Pt^{2+} takes 2 eV). A metal cannot lose or donate electrons to any other element that is less electronegative than itself. Therefore, an element that is much more electronegative than the metal you wish to dissolve or put into solution would be a logical choice as a solvent. Remember, electronegativity is the power of an atom in a molecule to attract electrons to itself.

Now let us look at some electronegativities (ENs) of various elements:

Platinum	2.2 EN	Gold	2.4 EN
Mercury	1.9 EN	Nitrogen	3.0 EN
Oxygen	3.5 EN	Fluorine	4.10 EN
Carbon	2.50 EN	Silver	1.9 EN
Sulphur	2.44 EN	Copper	1.9 EN
Chlorine	3.0 EN	Bromine	2.8 EN

Looking at the above ENs of some of the elements, it becomes evident that fluorine would be a good electron grabber and extremely useful in forming a molecule of gold fluoride, platinum fluoride, and so forth. In fact, fluorine with its EN of 4.10 is so active that it will combine with almost anything.

The reason it is not widely used to form molecules with precious metals in order to extract them is its high activity with so many elements. Fluorine mixed with water produces hydrofluoric acid, which will attack glass and silica along with most anything else.

Halogens

The halogen family consists of fluorine, chlorine, bromine, iodine, and astatine, all of which are poisonous. We call the halogen group the "take" elements because all of the outermost electron shells (the valence shells) of the group have 7 electrons and need only 1 more electron to complete the magic number. Remember, the closer this outer shell of 7 electrons is to the nucleus, the stronger the attraction is to capture an electron from an element with an electron a good distance from its nucleus, like gold and platinum. Gold has a single electron way out in the P shell and it is in the *s* subshell, a good distance from the gold nucleus, as does platinum.

Remember, the shells counting from the nucleus out are K, L, M, N, O, P, and Q. Fluorine has a nucleus of 9 protons and 9 electrons. These 9 electrons occupy only the K and L shells—2 in the K shell and 7 in the L shell. This is what makes fluorine such a hot electron snatcher with such a high electronegativity number of 4.10.

All halogens produce extremely active acids when they fill in their outer shell of 7 electrons to a full 8, with this eighth electron coming from hydrogen:

Fluorine plus H = Hf (hydrofluoric acid)
Chlorine plus H = HCl (hydrochloric acid)
Bromine plus H = HBr (hydrobromic acid)
Iodine plus H = HI (hydriotic acid)

All four are capable of (dissolving) forming salt molecules with platinum and gold. The word *halogen* means salt former. Thus, with any halogen plus an oxidizer, you can produce a soluble precious metal salt of gold or platinum.

Ruling out the halogen fluorine because of the problem of handling both the fluorine and the process, the next best bet is chlorine.

Chlorine

Remember, chlorine is diatomic—two atoms of chlorine forming a molecule of chlorine—and is always written Cl_2. Of the halogen families, the most used for precious metal extraction are chlorine (Cl_2) and bromine (Br). Chlorine was widely used for many years, as was bromine; then things moved to cyanide. Cyanide became the most used reagent for gold and silver extraction and is still widely used. However, chlorine is coming back into favor and bromine is becoming very popular again.

Some firms selling the so-called superleaches, new, just-discovered great breakthrough methods, are simply reinventing the wheel. Not long ago, there was a push to use thiourea as an extractant (leach), also with lots of "hoopla": just discovered and so forth. In fact, the Egyptians used camel urine for extraction of gold. Thiourea?

What we wish to do is simply move the platinum Pt° from ground state (metallic) to Pt^+, where it becomes a part of a salt molecule which is soluble in H_2O. Thus, we can wash it free of the gangue and then convert it back to ground state (metallic) by replacing the electrons it lost to the chemical reaction with a suitable reagent or electrons supplied from an outside source.

As NaCl (table salt) is a salt composed of a metal and a halogen (salt maker), in our case Cl_2, we are simply going to use platinum as our metal in place of sodium (metal) along with Cl_2 to give a water-soluble platinum chloride salt. If we evaporate off the water solution of $PtCl_4$, we sure enough wind up with a crystallized platinum salt—platinum chloride ($PtCl_4$), red crystals soluble in water and alcohol, produced by solution of platinum in aqua regia and evaporation.

Platinum tetrachloride ($PtCl_4$) is soluble in water; however, platinum dichloride ($PtCl_2$) is a greenish gray powder and is not soluble in water; it is only soluble in hydrochloric acid or ammonium hydroxide.

You have no doubt noted the oxidation-state difference of the platinum atom $PtCl_2$. Here we have snatched off 2 electrons from the valence shell of the platinum atom; therefore, the platinum atom has two more + protons in its nucleus than electrons, giving the atom (cation) a net gain of + 2 eV (78 positive protons and 76 negative electrons). With $PtCl_4$, we have added 2 more chlorine atoms to our molecule, each taking 1 more electron to fill out its outer shell with the magic number of 8 electrons. So, four chlorine atoms are happy and the gold atom is a loser of 4 electrons, making it now 78 + charges and only 74 − charges for a net gain of 4 positive. It could be stated as $AuCl_2 = Au^{2+}[Cl^-]_2$ and $AuCl_4 = Au^{4+}[Cl^-]_4$.

Mercury

Now, we have a better understanding of the platinum atom and how valence electrons operate in order to form various metallic salt compounds and why.

Of late, there has been a world of "hoopla" in regard to capturing platinum with mercury (Hg) and the electrocharged mercury apparatus being sold. True Pt particles can be wetted by what is referred to as sodium amalgam Na_xHg_x, which is simply mercury containing 2% to 10% metallic sodium.

If you take bone dry mercury, heat it to 200°C and drop small pieces of metallic sodium on the heated mercury (slowly) until 2% to 10% of the total is sodium, you have a sodium–mercury compound that will wet platinum. This material decomposes quite rapidly when wet. What happens is that the sodium decomposes the water and you wind up with hydrogen (g) mercury and sodium hydroxide.

Some devices to produce the so-called charged Hg are simply salt solution cells. These cells do not produce sodium amalgam; they produce chlorine, sodium hydroxide, and hydrogen. As far as benefiting the mercury, you might simply add some sodium hydroxide to it. There are a great many misleading items and information out there.

Compounds of Platinum

Pt^+ in gas phase	g	$Pt(OH)_2$	c
$PtCl$	c	$PtCl_2$	c
$PtCl_3$	c	$PtCl_4$	c
$PtCl4\cdot 5H_2O$	c	$PtCl_6$	aq
H_2PtCl_4	aq	H_2PtCl_6	aq
$H_2PtCl_5\cdot 2H_2O$	c	$H_2PtCl_6\cdot 6H_2O$	c
$PtBr_4$	c	$PtBr_6$	aq
H_2PtBr_6	aq	$H_2PtBr_6\cdot 9H_2O$	c
PtI	c	PtI_6	aq
PtS	c	PtS_2	c
$Pt(NH_3)_4(OH)_2$	aq	$PtCl_6\cdot 2NH_3$	c
$(NH_4)_2PtCl_4$	c	$Pt(NH_3)_4Cl_2$	c
$Pt(NH_3)_4Cl_2\cdot H_2O$	c	$PtCl_2\cdot 5NH_3$	c
$PtI_2\cdot 2NH_3$	c	$PtI_2\cdot 4NH_3$	c
$PtI_2\cdot 6NH_3$	c	$PtCl_2(NH_3)_4SO_4$	aq
$AgPtCl_6$	c	$AgPtBr_6$	c

NOTE: c = crystal; aq = aqueous; g = gas.

Separating the Platinum Group

There are many methods you can use. Let us say you have some cons from a table or other concentrating device; you could start out with an aqua regia leach which would leave you with Au, Pt, Pd, Cu, and so forth in colution, and Rh, Ru, Ag, and so forth, in the residue from this first leach.

In this case, you have a real complicated soup on one hand and a real complicated residue on the other. In a great many cases, this direct approach with aqua regia looks good, as you have side-stepped a few moves. However, both the leach and the residue contain worlds of unwanted elements which could "drive you up the wall" when you start to separate what you want from the two components: the liquid and residue. Also, your leach aqua regia can be rendered ineffective by unwanted elements in your starting material. There is no reason to list these here as that is not the way we are going to tackle the problem anyway.

The following material should all be treated the same way: concentrates, auto catlytic converters, electronic sweep, precious metal scrap, and photo film.

Our first move is to get a precious metal alloy which is free from everything else. The only way that you can accomplish this is by first smelting everything to lead bullion and then cupel to get the precious metal dorie we wish to separate.

Now, in an attempt to read your mind, you might say what about cyanide, thiourea, bromine, and so on leaches? Even here you must make an ion exchange back to precious and nonprecious metals and then smelt to lead to accomplish what we want. Even with extremely lean ore, there is no method to date other than gas phase transport extraction that can touch direct smelting. You can smelt up to 20 tons of ore to lead an hour in a cupola 10 ft tall with an 18 in. inside diameter for a coke to ore ratio of 1 to 20. In fact, if you are dealing with buffs, sweeps, and things of that nature, it is the only way you can possibly come out a winner.

A good bet is to buy scrap lead, granulate it, and use this to smelt your material; not only is it inexpensive but you can pick up any precious metal that the scrap might be carrying. I have purchased some scrap lead to smelt material carrying ¼ ounce of Au, only to find the lead I purchased has 1 ounce of Au per ton and 15 ounces of Ag per ton.

Five pounds of lead will collect 1 pound of gold; platinum and its sisters are extremely soluble in lead.

Through the years, jewelers who worked with precious metals separated their pan scrap. A bench or manufacturing jeweler works over a pan which catches fillings and granules made by sawing. In time, he has a collection of mixed dust and granules of Au, Ag, Cu, steel, Pt, Pd, Ir, and so forth. Usually, the separation they use is to first place everything in a steel gold pan, add some gasoline, ignite, and stir this mixture around. This procedure burns off any organic material, matches, paper, glue, and so on. What is left in the pan is mixed with water, and the light ash is carefully panned off. The remaining heavy metals in the pan are washed off into an Erlenmeyer flask or large beaker and covered with a mixture of one part HNO_3 (nitric acid) and two parts of water, and heated. This will put the base metals, silver and palladium, into solution. What did not go into solution, gold and platinum, is filtered off. The filterate is saved to recover any palladium and silver from it.

As platinum is only slightly soluble in cold aqua regia (one part nitric acid, three parts hydrochloric acid, and three volumes of distilled water), this would be our next step. We prepare sufficient aqua regia in a beaker and chill it to 45°F. The gold and platinum mix is added and stirred every so often. The gold will go into solution, but only a minor amount of the platinum will go into solution. The platinum is filtered off and dried. The gold is precipitated from the aqua regia filterate by adding a 65% solution of hydrazine, drop by drop, until the gold drops out as a brown powder.

The remaining dry platinum is simply sprinkled on assay lead melting in a scorifying dish and brought to a red heat. The platinum is very, very soluble in hot lead. The lead containing the platinum is poured into a prill and cupelled.

The resulting bead is platinum which you refine to increase its fineness by the classical wet method as outlined in this book.

Au, Ag, Pt, Pd, Rh, Ir, and Os

Let us assume you have smelted to lead (collected your values in lead bullion) and have by cupellation come up with a piece of dorie which you suspect or know contains Au, Ag, Pt, Pd, Rh, and Ru. Now let us take the dorie and peel it like an onion. It is not hard to do if you take it step by step as I instruct; do not deviate (leave out a step) and you will get good results.

Do not undertake to part a large amount of dorie the first time. The first run is to familiarize yourself with the process. Once you have gone through a multiple parting a few times, you will soon know which steps to delete based on your starting dorie. It would be rather foolish to run a dorie which is 99% Au, Ag, or Pt. Through the entire process, you pick and choose, depending on your starting material. Also, it becomes quite evident when running a batch of unknown from which you get nothing at a particular step that you should stop going in this direction any further. Let us assume that we have a dorie from our cupellation that we know consists of a mixture of Au, Ag, Pt, Pd, Rh, Ru, and Ir.

Step by Step

We digest our dorie in hot aqua regia (one part nitric acid, three parts hydrochloric acid, and three volumes of distilled water) and filter off the residue onto a filter paper. The solution contains the Au, Pt, and Pd. Set this aside. The residue contains Rh, Ru, Ir, and Ag.

Rh, Ru, Ir, and Ag Residue

This residue is left on the filter paper to dry. When dry, it is placed in a porcelain crucible and covered with granulated 0.999 fine assay lead smelted at 1500°F in your assay furnace or over a good Bunsen burner until the Rh, Ru, Ir, and Ag are absorbed into the lead. The lead containing the Rh, Ru, Ir, and Ag is poured into a prill, which is then cupelled in a bone ash cupel to give you a dorie bead which now contains Rh, Ru, Ir, and Ag as metallics.

Parting Again

This bead is dissolved in hot HNO_3 (½HNO_3 ½H_2O). The HNO_3 solution is brought up to nearly boiling and the bead is dropped in; this is best done in a porcelain parting dish. You now have a solution containing the Ag and possibly some Pb. The residue left in the dish contains Rh, Ru, and Ir, which you filter off onto a filter paper. Mark this paper Rh, Ru, and Ir and set it aside to dry. Let us get rid of the HNO_3 solution first.

HNO_3 Solution Containing Ag and Pb

Heat this solution just below boiling and add a few milliliters of H_2SO_4 and heat for 4 or 5 min. You will notice that you again have a solution and a residue after this treatment. The residue is $PbSO_4$ (lead sulfate, white lead). The approximate formula is $PbSO_4 \cdot PbO$. The solution is an aqua solution of Ag_2SO_4 (silver sulfate).

Filter off the $PbSO_4$ onto a filter paper. When dry, this white lead can be thrown back in your lead fusion the next time you smelt your Rh, Ru, Ir, and Ag residue.

To the solution of Ag_2SO_4 simply add enough HCl to drop the silver down as chloride. This can be melted down with charcoal under Na_2CO_3 to an impure silver button. Of course, you can further refine the silver by electrolysis if you choose.

The Rh, Ru, and Ir Residue

This dry residue along with the filter paper is fused with $NaHSO_3$ (sodium bisulfate). This fusion should also be done in a porcelain-glazed crucible. The fusion is not dissolved in hot water. At this point, you have the Rh in solution as $Rh_2(SO_4)_3$, and the residue from your H_2O extraction is Ru and Ir. Filter off the Ru and Ir residue.

Rh Solution

Add NaOH (sodium hydroxide) to the solution containing the Rh. It is not $Rh(OH)_3$ (rhodium hydroxide). At this point, you add HCL (hydrochloric acid). Then treat this with $NaNO_2 + KCl$ (sodium nitrite + potassium chloride). Filter off this precipitate, which is $K_3(Rh(NO_2)_6$ (potassium rhodium nitrate).

You now treat this HCl (hydrochloric acid), which gives you potassium rhodium chloride (K_2RhCl_6). You can, at this point, go back to square one and again fuse

K_2RhCl_6 with $NaHSO_4$ (sodium bisulfate) and repeat everything back down the line again to K_2RhCl_6. This will purify your product.

Some small refiners sell the product at the point where you arrive at K_2RhCl_6, the potassium rhodium chloride, without repeating the purification process. You can, at this point, ignite K_2RhCl_6 in H_2 gas which will reduce the rhodium salts to Rh metal; or use a platinum anode, dissolve the salts in distilled water, and plate the Rh out.

Residue of Ru and Ir

This residue is from the H_2O extraction of the $NaHSO_4$, which was our Rh, Ru, and Ir fusion.

The filtered off residue of Ru and Ir is fused with KOH + KNO_3 (potassium hydroxide + potassium nitrate). This fusion is also done in a porcelain crucible. At this point, we do an extraction of this fusion with hot distilled water. This gives us a solution and residue. Filter the residue off onto a filter paper. This residue is Ir. The Ru is in the solution as $KRuO_4$.

Let us take the Ir residue first. Fuse this Ir residue with NaO_2 (sodium dioxide). This fusion is extracted with aqua regia. The extraction gives $IrCl_4$ (iridium tetrachloride). By adding NH_4Cl (ammonium chloride), you will get a precipitate of $(NH_4)_2$ $IrCl_6$ (ammonium iridium chloride). This can be redigested for further purifying or simply ignited in H_2 to give you iridium metal.

Solution Containing $KRuO_4$

This is the solution we got from our extraction with H_2O of our KOH + KNO_3 fusion which contained Ru and Ir.

To separate the Ru from our extraction solution, we are going to take it off as a gas phase. To do this, we will have to oxidize the solution at the boiling point with Cl_2 (chlorine gas) which produces RuO_4 (ruthenium tetraoxide gas). This gas is treated with HCl, giving $RuCl_3$ or ruthenium trichloride. This can be ignited in H_2 to give Ru.

Osmium

No, I did not forget osmium. Let us back up to our solution containing $KRuO_4$, and say that in this solution that we have some osmium which came from our original dorie metal at the very start. Here is an alternate way to treat the solution which we just covered in the previous subsection. Only now let us say we have Ru and Os in the solution.

Add CH_3OH + HCl (methyl alcohol + hydrochloric acid) in a distilling flask fitted with a condenser, and slowly distill off the liquid. The residue left in the flask is $RuOCl_2$. The product distilled across and in the receiver is OsO_4 (osmic acid anhydride). This entire operation must be carried out in tight-fitting glassware in an approved fume hood.

NOTE: Osmium and ruthenium, when heated in air, form volatile oxides. These oxides can be captured and reduced back to metallic form without much difficulty. Osmium oxide is extremely dangerous. If osmium oxide touches the mucous membrane of the eye, it breaks down and deposits a film of metallic osmium in the tissues. More than one operator has been blinded by osmium oxide fumes. One should never work with any metal without the proper hooding and other safety devices.

Au, Pt, and Pd in Solution

Go back to the subsection entitled Step by Step. In our first step, we set aside our solution of aqua regia which contains Au, Pt, and Pd in solution. Now let us peel the solution. Boil this solution to a thick syrup, add hydrochloric acid, and boil it down again to a thick syrup. Do this at least three times. This is to expel the nitric acid. If we did not do this and completely expel the nitric, we would always be dealing with aqua regia, and when we try to drop our gold, it will redox. In other words, it will drop out as a cloud of brown precipitate (gold) but will reoxidize and go back into solution:

$$\text{Au cationic} \rightarrow \text{Au metal}$$
$$\text{Au cationic} \leftarrow \text{Au metal}$$

Remember from your study on valence bonding, we removed an electron from the gold to put it into a soluble cation, Au^+, using nitric acid as an oxidizer in hydrochloric acid, producing a soluble gold chloride salt. Remember, chlorine is a halogen, a salt maker. So we have the gold salt dissolved in an aqua regia solution, the gold cations (plus charged gold ions) swimming around, each missing an electron which we wish to replace to make the gold cation go back to a gold atom of metal. If we supply a chemical reagent to supply these needed electrons to do this, the solution must be in such a chemical condition (a nonsolvent of gold); otherwise, we will drop out the gold, only to have the solution put it back into solution. This is why we must get rid of the nitric acid.

If this operation is not completed properly and the gold redoxes back into solution, you have to boil the solution back down to a syrup and add HCl (hydrochloric acid) and repeat this three or four times.

Dropping Out the Gold

Having successfully expelled the nitric acid from our aqua regia, the thick syrup from our third or fourth boil down is now diluted with one or two volumes of distilled water. Heat this solution to approximately 90°F and bubble SO_2 gas (sulfur dioxide gas) into this solution slowly until all the gold drops out.

Allow the gold to settle, decanter off the liquid, and filter off the gold and set it aside to dry. The solution now contains platinum and palladium in solution.

Pt and Pd Solution

This solution is heated to 80°F or 90°F. Make up a saturated solution of NH_4Cl (ammonium chloride), add this solution a little at a time to the hot Pt and Pd solution, stirring with a glass rod. The platinum will precipitate out as a hexachloroplatinate, $PtCl_6$, an orange powder.

This orange powder is collected on a filter to dry. Heat the dry powder in a porcelain-glazed evaporating dish. Do not get it too hot. You only want to see light white smoke coming off. This converts your orange powder to platinum metal. If you overheat to where you get dark smoke coming off your orange powder, there goes your platinum, bye-bye.

Solution Containing Palladium Ions

This is the filtered solution from our platinum orange drop. Place this solution in a casserole or a tall beaker. Give yourself lots of beaker height above the hot solution to prevent a boil-over. Add a few crystals at a time of sodium chlorate ($NaClO_3$) to the hot solution. Do this under the hood, as it gives off chlorine gas. You will soon see palladium–ammonium chloride, a red powder forming on the surface and sides of the beaker. Keep adding $NaClO_3$ until no more red powder comes down. This is filtered off and dried. It is reduced to palladium sponge exactly as you did with the platinum orange.

A word here on ammonium chloride and sodium chlorate. Buy these two reagents in small quantities and the best reagent grade possible, otherwise they may be contaminated and you get no results or poor results.

Repurifying

Repurifying is simple if you redissolve the gold that you recovered in fresh aqua regia and go through the process of recovering it from the solution, expelling the nitric acid over and over, and dropping the gold out with SO_2. Each time you do this, the purity of your gold goes higher. This is true with the other metals you have parted from your dorie or whatever material you had originally.

If you distill mercury with a retort and condenser, it is called distilled mercury. If you distill again, it is called double distilled, and again it is triple distilled. There is a great difference in price between distilled mercury and triple-distilled mercury.

If you are looking for gold that is puratronic 99.9999% fine, you are looking at a price somewhere around $1200 for 25 g. Mercury, redistilled 99.998% pure, would be somewhere close to $32.40 for 450 g. For puratronic 99.999995% pure mercury, the same 450 g would be somewhere near $171.00.

There is a definite point of diminishing returns. It is simply how far you wish to purify.

There are many other ways to go from your dorie to a point where you have each constituent (metal) separated and off to itself. The method I have outlined is the one I prefer and is the classical chemical method most used. There are a great deal of so-called secret formulas out there touted to perform very well. Beware of activated mercury and leach chemicals with strange names like PGQ, SDPS, and so forth. Once you understand chemical bonding it will not take you long to determine what reaction will take place under what conditions and what the results will be.

A copy of *Chemical Technician's Ready Reference Hand Book* by Shugar, Shugar Bauman, and Bauman and published by McGraw-Hill Book Co. is an indispensable help for anyone without chemical bench experience; a handy reference regardless of your chemical background. It covers all types of lab equipment and its operation, loads of tables, and so forth.

Now, refer back to the subsection entitled Dropping Out the Gold. As with any reagent used to precipitate metallic ions out as metallics, you can run into coprecipitation. In our case, when using sulfur dioxide (gas), there is always the likelihood of bringing down some of the Pt and Pd along with the gold—in which case reprecipitation is necessary. In that case, use hot oxalic acid. If you are below 10 mg of gold in your cooked-down aqua regia solution, reprecipitation by hydroquinone will do a good job.

In place of SO_2 gas, some operators use sodium sulfite to drop the gold. However, when using sodium sulfite, you must remember you are adding alkaline salts which might cause problems in subsequent treatments.

Os and Ru from Pb Button

You can recover the Os and Ru from your starting lead button you produced in the subsection entitled Au, Ag, Pt, Pd, Rh, Ru, Ir, and Os. In this case, you do not cupel the lead button to dorie. You can digest the lead button in a distilling flask with perchloric acid and capture the values of Os and Ru in a train of chilled receivers.

The Game

It is a game of what is soluble in what, and what will precipitate what out of what solution. You have many solvents and combinations of solvents to choose from, knowing approximately what you have to digest, its ionization potential, and its electronegativity and valence. Looking at this plus your selection of solvent, it is quite easy to make a choice.

First look at the atom—what its valence is, and where the valence electrons are with respect to the nucleus (distance). Remember, the closer the outermost valence electron or electrons to the nucleus, the tougher it is going to be to snatch them away to enter into a chemical reaction. Most people engaged in extractive metallurgy classify this field of endeavor as inorganic chemistry. This is really not the case. It is more like organometallic chemistry. Get a simple beginning text in organometallic chemistry. Once you read it, the connection will become apparent.

Gas Phase

Gas phase (or gas transport) extraction of platinum and palladium is a good way to go. However, the initial setup is quite expensive. It would be the subject of quite a lengthy article in itself, but I feel that at least I should touch on it.

Very simply, if you subject a metal particle to a stream of a halogen gas under the proper conditions, the metal will be converted to a volatile gas molecule and transported from the gangue into a condenser where it can be recovered and converted to metallic form (Au°, Pt°, Pl°).

It is unlike vacuum plating of precious metals, where you bring the metal you are plating with up to and above its vaporizing temperature in a vacuum chamber, and the vaporized metal upon striking any surface below its vaporization temperature coats that surface with the metal. With gas-phase extraction, you are not vaporizing the metal but creating the conditions whereby the metal atoms are excited, placing the valence electrons a sufficient distance from the nucleus, thus making them easy prey for any halogen atoms to couple up with the metallic atoms to produce a metal halogen molecule (salt). This salt will and does have a much lower vaporizing temperature. If you pass Cl_2 rapidly over gold at 240°C, Au_2Cl_6 (gas) is formed. When cooled, it sublimes to give red crystals (Au_2Cl_6 crystals). If you then vapor transport Au_2Cl_6 in an atmosphere of chlorine at 247°C, AuCl crystals are deposited in the cold end of your reactor. The same is true of Pt and Pd. It is becoming more and more the process of selection in the recovery of platinum and palladium from crushed ore concentrates and is widely used to extract Pt and Pd from scrap spent automotive catalysts. Why it is not more commonly used for Au, Ag, and so forth, is beyond me. It is not really new tech; it has been around for years and years. Most operators use mixed gases to do the trick.

Some Mixed Gases Common Used in Gas-Phase Extraction of Precious Metals from Concentrates

50% Cl_2
5% Co
45% Ar

50% Cl_2
50% Ar

95% Cl_2
5% Air

9% CCl_4
91% Air

95% Cl_2
5% CO

90% F_2
10% HF

20% $COCl_2$
80% CO_2

I have had very good success using 9% CCl_4 (carbon tetrachloride) and 91% air in gas-phase assaying of various ores. Some assays that show only a trace of value by standard fire assay will show in the ounces per ton numbers when assayed via gas-phase extraction.

Summing Up

It is not enough to know that in order to separate a mixture of, say, salt and pepper one from the other, if you put your salt and pepper in water, the salt will dissolve in the water and the pepper will not and can be removed by filtering it off. You should know exactly what is taking place: how the water dipoles break the bonds between the sodium and chloride and why this happens. Also, how you carry the salt and pepper mix further if you like and wind up with pepper, chlorine (gas), and metallic sodium.

If you put some Pt and Pd in solution with dilute hydrochloric acid, using hydrogen peroxide as an oxidizer and place a sheet of aluminum in the solution, the Pt and Pd will precipitate out, with the aluminum taking its place. Why?

Before taking on any process or equipment to perform the extraction or recovery of precious metals, always ask these questions first. How does this process or equipment do its thing chemically and mechanically? If the answers do not agree with classical chemical reactions, beware. The so-called secret formulas for extraction are all over the place. Some are pure fraud and others are commonplace chemical elements or compounds, disguised as a major breakthrough and given a new name or initials and numbers. They are then sold at 4–10 times the price you could buy them from your local chemical supplier.

The ads for these products all seem to carry terms like New, Breakthrough, Super, Bidegradable, Nontoxic, Noncyanide, Just discovered, Activated, and so on. Sodium bromide (NaBr) is sold under some 50 different disguised names as a precious metal solvent, as is $NaBrO_3$ (sodium bromate), a very strong oxidizer (O_3).

Valences of Some Common Elements and Radicals

Name	Symbol	Valence	Name	Symbol	Valence
Aluminum	Al	+3	Hydrogen	H	+1
Ammonium	NH_4	+1	Lead	Pb	+2
Barium	Ba	+2	Magnesium	Mg	+2
Calcium	Ca	+2	Mercuric	Hg	+2
Chromium	Cr	+3	Mercurous	Hg	+1
Cobalt	Co	+2	Nickel	Ni	+2
Cupric	Cu	+2	Potassium	K	+1
Cuprous	Cu	+1	Silver	Ag	+1
Ferric	Fe	+3	Sodium	Na	+1

Name	Symbol	Valence
Ferrous	Fe	+2
Acetate	$C_2H_3O_2$	−1
Bicarbonate	HCO_3	−1
Bisulfate	HSO_4	−1
Bromide	Br	−1
Carbonate	CO_3	−2
Chlorate	ClO_3	−1
Chloride	Cl	−1
Chromate	CrO_4	−2
Ferricyanide	$Fe(CN)_6$	−3
Ferrocyanide	$Fe(CN)_6$	−4
Hydroxide	OH	−1
Zinc	Zn	+2
Hypochlorite	ClO	−1
Iodine	I	−1
Nitrate	NO_3	−1
Nitrite	NO_2	−1
Oxide	O	−2
Permangate	MNO_4	−1
Phosphate	PO_4	−3
Sulfate	SO_4	−2
Sulfide	S	−2
Sulfite	SO_3	−2
Tartrate	$C_4H_4O_6$	−2

6

Electrochemical Principles

This chapter discusses electrorefining cells and the chemical–electrical principles that make them work.

Ionization

S.A. Arrhenius, in 1887, attempted to explain the abnormally high osmotic pressures exerted by many aqueous solutions. He discovered that only solutions that conduct current exert high osmotic pressures. From this, he deduced that some sort of particles other than molecules were present in these solutions, and he designated them by Faraday's term "ions." Osmotic pressure is the most convincing proof of ionization.

Simply explained, ionization is the formation of ions. If you dissolved table salt (sodium chloride) in water, the elements sodium and chlorine would dissociate in the water solution into ions—positive ions called cations and negative ions called anions. A sodium chloride molecule is a compound of one sodium atom bound to one chlorine atom. Sodium (Na) has a valence of + 1, so its ions are cations; chlorine (Cl), as a chloride, has a valence of – 1, so its ions are anions. See Figure 6.1.

In the case of dissolved sodium chloride, each atom in the original molecular compound becomes a separate ion in solution, but this does not always happen. Cupric sulphate ($CuSO_4$) (a copper salt), when dissolved in water, produces Copper (Cu^{2+}) ions and sulphate (SO_4^{2-}) ions; the sulphur (S) and oxygen (O) atoms do not each form separate ions.

Ionization is always reversible. You can remove ions as a solid or as a gas. You can also replace ions, putting one type into solution to drop out the desired type (as a solid). You may remember that if you hang a piece of clean copper in a nitric acid solution containing silver ions, the copper will begin to dissolve,

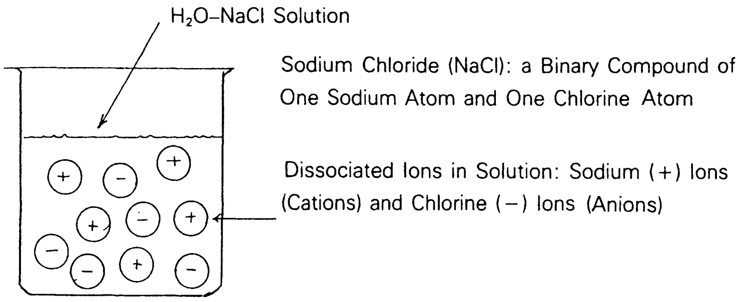


Figure 6.1. Dissociated ions in a solution

throwing copper ions into the solution, while silver ions come out of solution and attach to the remaining copper as metallic silver crystals. This action is called ion exchange; it goes on without benefit of an outside electrical current and is based on the electrical potential differences between the ions involved.

Single Electrical Potential

The accompanying table shows the approximate single electrical potential of metallic elements toward solutions with normal metallic ion concentration or activity, based on hydrogen as 0 V. Each metal will replace the ions of any metal in solution that is more noble (or more electrically positive) than itself. For example, zinc ions (at – 0.76 V) will replace cadmium ions (at – 0.40 V) because the cadmium ions are more positive than the zinc ions.

When an ion comes into contact with an ion that is more negative than itself (assuming that the solution is in equilibrium, it is neutralized and reconverts to metallic form. This is the principle behind precipitating gold ions out of an aqua regia solution with ferrous sulphate. Iron has a single electrical potential of –0.44 V, and gold a single electrical potential of + 1.36 V.

Single Electrical Potentials of Some Metallic Elements
(Hydrogen 0.00 V)

Negative		*Positive*	
Aluminum	–1.71 V	Antimony	+0.10 V
Zinc	–0.76 V	Bismuth	+0.20 V
Chromium	–0.56 V	Arsenic	+0.32 V
Iron	–0.44 V	Copper	+0.34 V
Cadmium	–0.40 V	Rhodium	+0.68 V
Indium	–0.34 V	Mercury	+0.78 V
Cobalt	–0.28 V	Silver	+0.80 V
Nickel	–0.23 V	Platinum	+0.90 V
Tin	–0.14 V	Gold	+1.36 V
Lead	–0.12 V		

It will be of great benefit to you to do additional study on ions and osmotic pressure.

Electrolysis

Electrolysis is the chemical decomposition of certain substances by means of an electrical current that is passed through the substances while they are in a dissolved or molten state. When you apply an external DC electrical current to a solution containing positive and negative ions, you initiate electrolysis. The solution is called the electrolyte. In refining and extraction, the term "pregnant solution" is often used to refer to a solution containing metallic and other ions.

An extremely simple pregnant solution can be made by dissolving a copper salt [for example, copper sulphate ($CuSO_4$)] in water and adding the corresponding acid of the salt [in this case, sulphuric acid (H_2SO_4)] to increase the conductivity of the solution. To make copper sulphate, dissolve copper in dilute sulphuric acid and then, in a cool place, let the solution evaporate in a shallow evaporating dish; you will be left with water-soluble blue crystals, granules, or powder (copper sulphate). This salt has a metal (copper) content of approximately 25.5% (by weight).

Dissolve about 15 ounces of copper sulphate in ½ gal of warm distilled water. To this, add about 2 fluid ounces of full-strength sulphuric acid. You now have a simple acid and copper ion electrolyte.

The chemical equation for the separation of copper sulphate in dilute sulphuric acid is $CuSO_4 \rightarrow Cu^{2+} + SO_4^{2-}$. The left-hand side of this equation represents only the chemical elements involved in the electrolyte. The right-hand side shows that, in the sulphuric acid solution, the Cu^{2+} ions and the SO_4^{2-} ions are dissociated and move around in the solution at random until influenced by the addition of a reagent, such as zinc, or by the application of an electromotive force (electrolysis).

Place the solution in a large beaker on the hot plate. You will need a source of DC current—a battery, a rectifier, or a DC generator. In this illustration, start with a fully charged 6-V lead acid automobile battery, a voltmeter, an ammeter, and a rheostat. Set them up as shown in Figure 6.2.

Attach a stainless steel plate to the positive wire; this is the anode. Attach another stainless steel plate to the negative wire; this is the cathode. Partially submerge both plates in your copper sulphate electrolyte. When we close the switch, applying an electrical potential across the solution between the two stainless steel plates, the positive ions (Cu^{2+}) head for the negative plate. When each of these copper ions, carrying its double load of positive charge, makes contact with the negatively charged stainless steel plate, the + + charge it carries is canceled out by the negative plate, and the Cu^{2+} ion is converted into a red metallic copper deposit on the cathode. While this is going on, the negative ions (SO_4^{2-}) are headed for the positive plate, the anode. When they get there and make contact, they lose their electrons (the – – charges) and become radicals.

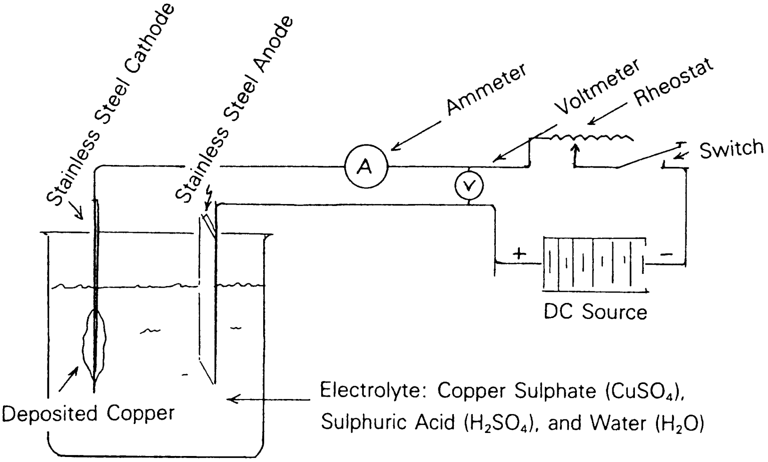


Figure 6.2. Simple copper-plating setup

This entire action could be described as a chemical reaction produced by miniature short circuits of + and − ions with positively and negatively charged plates. See Figure 6.3. The electrical force in this case could be called a catalyst, as it causes a chemical reaction but is itself unchanged by the reaction.

The electrical and chemical changes that occur during electrolysis are represented by electrochemical equations in which ions carry charges equal to their chemical valence.

The electric charge carried by a gram equivalent weight of any element or radical is 96,540 C. A coulomb is that quantity of electricity which flows across

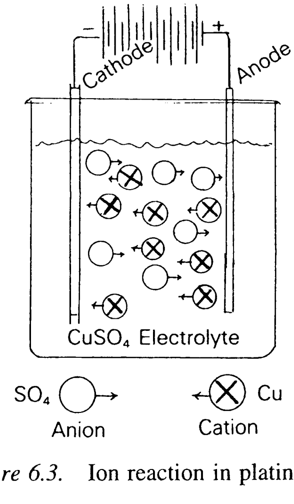


Figure 6.3. Ion reaction in plating cell

a conductor when a current of 1 A is maintained for 1 s. To liberate 1 g of hydrogen gas by the electrolysis of water, you must supply 96,540 C of electricity. The quantity of electricity required to produce a gram equivalent weight of chemical change is known as a Faraday and is the same for all metals: 96,540 C.

If you allow your cell with the copper ion electrolyte and the stainless steel anode and cathode to continue to run, it will simply strip the solution of values. This is one of the principles behind electrochemical systems of recovering values from pregnant cyanide or acid solutions in primary metal extraction. The metal can be deposited on steel wool or on pure metal cathodes. There are numerous physical arrangements of cells possible for accomplishing this. See Figure 6.4.

If you replaced the stainless steel anode in your simple cell with a copper anode, you would have provided the basis for electroplating and electrorefining. Unlike the stainless steel anode, which is not soluble in the electrolyte, a copper anode would be soluble in the electrolyte and would provide a continuing supply of copper ions to the cathode. See Figure 6.5.

The loss of positive charges due to the neutralization of Cu^{2+} ions as they come in contact with the negative cathode is offset by the entry into solution of new copper ions obtained at the anode.

The electrons drawn up from the anode travel through the external circuit to the cathode and, by doing so, are available for the neutralization of newly arriving Cu^{2+} ions at the cathode. What this amounts to is a simultaneous redox process:

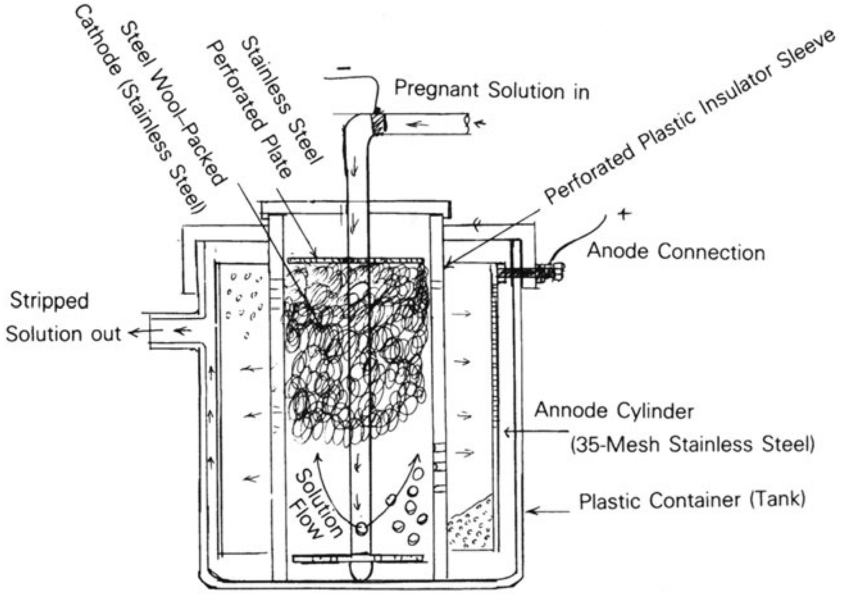


Figure 6.4. One type of steel wool electrolytic cell

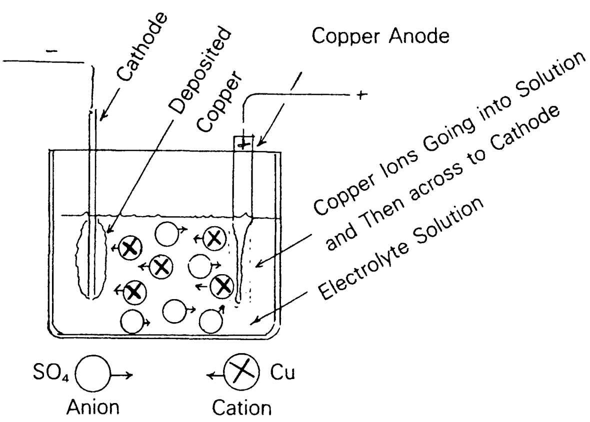


Figure 6.5. Simple copper cell

At the anode, you have oxidation reactions, and at the cathode, reduction reactions. See Figure 6.6.

In actual electrorefining, the chemical composition of the electrolytes must be maintained very carefully: You must maintain a certain level of free or available acid in acid electrolytes and of free cyanide in cyanide electrolytes, as well as a certain level of ionic concentration. This is true whether you are stripping a pregnant system using an insoluble anode and cathode, or are refining from an impure anode to a pure cathode, or are refining from an impure anode to an insoluble cathode.

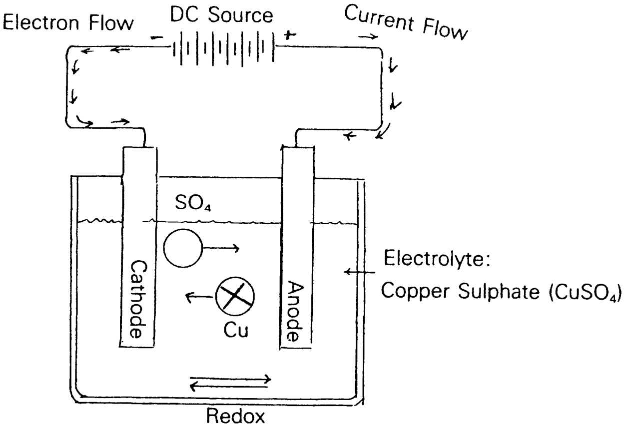


Figure 6.6. Redox in electrolytic cell, showing electron flow and current flow

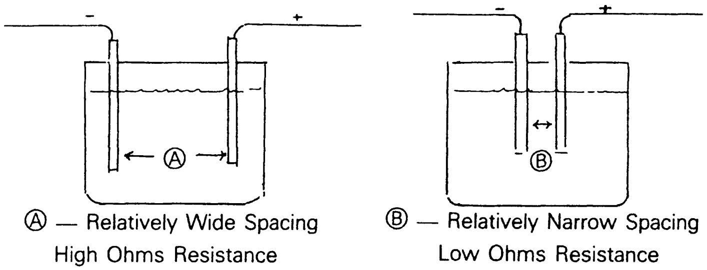


Figure 6.7. Resistance of electrolyte as a function of cathode–anode spacing

Cell Voltages

Whether you plan to make a solution-stripping cell or a refining cell, there is a definite potential difference in volts that you must establish in order to overcome the equilibrium potential of the cell. Equilibrium potential is normal resistance (in ohms) of the system at rest to the flow of applied current. You must overcome the resistance in the electrolyte itself, which will vary proportionately with the space between the cathode and the anode, the ionic concentration, and the free cyanide or acid in the bath. See Figure 6.7.

Another factor that slows the migration of the + ions to the cathode and the – ions to the anode is the attraction of the + and – ions to each other in the solution. See Figure 6.8.

There is no precise correlation between the amount of metal stripped from a solution and deposited on the cathode and the voltage applied across the cell; as I said, this depends on the ionic concentration and the solvent. For example, the

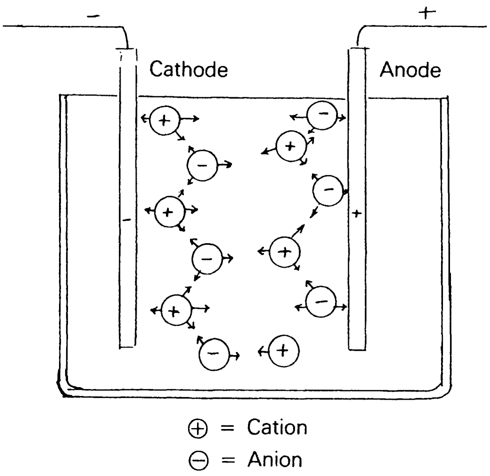


Figure 6.8. Mutual attraction between positive and negative ions in solution

voltage required for the decomposition of silver as a nitrate (nitric acid solvent) is 0.7 V, as a sulphate (sulphuric acid solvent) it is 0.8 V, and as a chloride (hydrochloric solvent) it is 0.84 V. The voltage required for the decomposition of zinc as zinc sulphate is 2.5 V, and as zinc chloride it is 1.38 V.

Polarization, simply defined as an increase of resistance to an electrical flow through the electrolyte that is caused by the accumulation of gaseous molecules on the electrodes, is another problem. Polarization can render the electrodes partially or completely insulated, slowing down or stopping the flow of current through the cell. The gaseous molecules or bubbles that form are usually composed of hydrogen.

Finally, you also can have problems with the speed of the ions through the solution. If the ions cannot move to the cathode as fast as the reduction to metal is taking place, the cathode will reduce the ions at its face faster than the new supply can arrive and will quickly be left with no + ions to reduce.

This situation leads to a condition that is called concentration polarization. When the speed of reduction at the cathode is greater than the speed of arrival of the replenishing supply of + ions, the cathode will cause the pH of the solution around the cathode to rise, precipitating unwanted basic salts in the electrolyte that result in a fouling of the bath (electrolyte) or a contamination of the refined metal product or both. The space around the cathode where this takes place is called the Nernst layer or Nernst diffusion boundary layer. See Figure 6.9.

You can combat this condition by stirring the solution, circulating the solution, and increasing the temperature of the bath to increase ionic activity. Another method is to periodically reverse the cell's polarity, manually or mechanically. See Figure 6.10.

The problem of hydrogen gas (H_2) evolution at the cathode is the most serious one in terms of preventing the arrival at the cathode of fresh + ions to be reduced. This condition forces you to increase the voltage of your cell in order to overcome its insulation effect. You must, then, overcome not only an equilibrium value

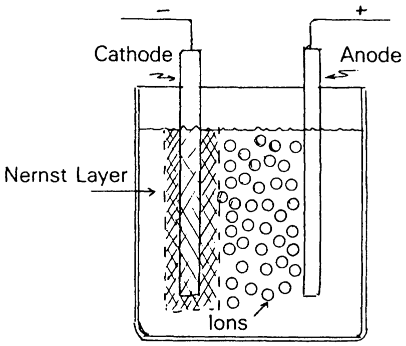


Figure 6.9. Nernst layer around cathode

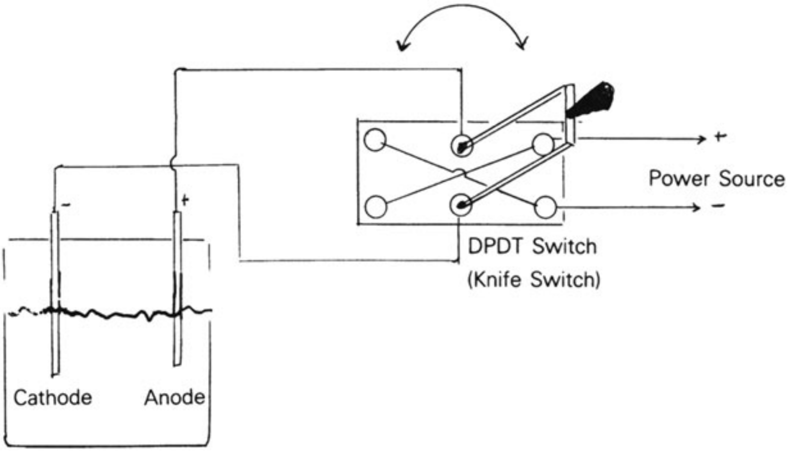


Figure 6.10. Polarity-reversing (DPDT) switch hook-up

(electrical potential) for the electrolyte but also the potential that causes the evolution of hydrogen gas bubbles. This potential is known as hydrogen overvoltage.

Some relative hydrogen overvoltages are smooth platinum—0.068; gold—0.39; electrolytic iron—0.56; copper—0.58; carbon—0.7; zinc—0.75; nickel—0.76; silver—0.76; and lead—1.0. These values are only illustrative; they vary with the electrolyte, the current density, and the surface condition of the metal.

When hydrogen bubbles are evolved at the cathode (or oxygen bubbles at the anode), the potential that must be overcome almost always requires a greater change in voltage than does the potential corresponding to a change in the pH of the solution.

Unlike the solutions used in electroplating for cosmetic or other similar reasons, the solutions used in electrostripping or refining (where looks do not count) are simple and work over a reasonably broad range while still giving the desired results. In the electrorefining of a silver doré bar, for example, the electrolyte is silver nitrate and the anode (doré) is relatively impure, whereas in a high-quality silver-plating setup, the silver is pure and the electrolyte is a carefully formulated complex solution—such as silver cyanide (AgCN), potassium cyanide (KCN), free cyanide (CN), potassium carbonate (K_2CO_3), and carbon disulphide (CS_2) all in precise amounts and kept under precise control.

7

Electrorefining

In Chapter 6, I gave an illustration (Figure 6.4) of a cell that can be used to strip a solution of its values by depositing them onto steel wool. The problem here is that unless the pregnant solution is carrying only one type of metallic ion (such as gold or silver), you are going to have to part and refine the precipitate by wet chemical means or by an electrolytic cell anyway.

If you were to percolate a weak solution of cyanide through a mass of crushed ore, with enough oxygen present, various metallics would go into the solution as dissociated metallic cyanide ions—gold, silver, copper, and iron.

At this point, you are much better off precipitating the metallics using zinc ion exchange (cementation) than to try to separate them by electrorefining. Using cementation, you can remove most of the undesired base metals easily by (wet) selective parting or by roasting, and then melt up the remainder into a nearly pure doré bar, which you can refine by electrolysis. The choice is yours; however, with precious metals, the less pure the doré bar is, the less likely you are to see a profit.

With electroplating, you can ensure that the plating bath contains no metallic ions other than the ones you desire by dissolving a salt of the metal in the otherwise metal-free bath and by using a pure anode.

The pure anode, if everything is working correctly, will maintain the right number of metallic ions in the bath by going into solution and replacing the ions being reduced to metallic plate at the cathode. The cathode in this case is the object that you wish to have plated. It can be a metal object or a nonmetal object that has had its surfaces made conductive.

Electroplating anodes are of high purity to avoid fouling the bath or giving an off-color or a poor grade of plating. These high-purity anodes are usually the product of electrolytic refining. There are some situations in which two different metallic anodes are used in a special bath to produce an alloy deposit. This is called co-deposit plating. A typical brass plating bath consists of cuprous cyanide, zinc cyanide, and sodium cyanide (free cyanide). Using a zinc anode and a copper anode, each with its own separate voltage rheostat, you can plate brass in a wide variety of colors with this type of bath and with variations in the free cyanide, the pH, and so forth.

The exception to the rule of plating with a pure anode is chrome plating. The anode in this case is insoluble and the chrome comes from a chrome acid bath. There has been some work done on electrolytic extraction of chrome ores from baths made of chromic sulphate, chromous sulphate, and sodium sulphate.

The case of electrolytic refining is somewhat different: The anode is impure and you want only the desired metallic ion to plate across, leaving behind the impurity. The impure residue can, on occasion, contain some values. In the case of electrorefining, the reason for wanting the anode (the metal doré) to be as pure as possible is one of economy.

Electrolytic Copper Refining

Electrolytic copper can be produced from primary copper, secondary copper, or a combination of the two. The primary type comes from copper ore and is brought to the stage of crude impure copper by various primary copper recovery methods—leaching, crushing, smelting, or poling. The secondary type comes from scrap wire, electronic scrap, inexpensive gold-filled jewelry, eyeglass frames, and so forth. The crude copper is mixed with secondary copper scrap and cast into huge anodes. The mix is figured to give a cast anode of approximately 96% copper, the remainder being precious metals with traces of many other elements—such as zinc, nickel, and tellurium—depending on the source.

A great amount of today's primary gold recovery is from copper refining, where the gold values exist in the copper ore. The cells for electrolytic refining carry a great many anodes and cathodes and support a large-volume business. However, a single-anode and single-cathode cell will serve to illustrate their operation. See Figure 7.1.

The crude copper is the anode, and a pure copper starting sheet is the cathode. The electrolyte is made by dissolving, in distilled water, copper sulphate ($CuSO_4$), a copper salt that is approximately 25% copper. Some sulphuric acid is added as free acid to increase the conductivity of the bath.

A typical copper-refining acid bath, in miniature, would be 250 g/L of copper sulphate, and 75 g/L of sulphuric acid, a bath operating temperature of 70–120°F, a voltage of 6–8 V, and a current density in amperes of from 20 to 100 A/ft^2 of cathode surface.

Copper from the crude copper anode goes into solution and the positive ions of pure copper (Cu^{2+}) are carried over to the cathode by electromotive force through the electrolyte, where they are neutralized and build up as pure electrolytic copper on the cathode. The elements contaminating the crude anode fall to the

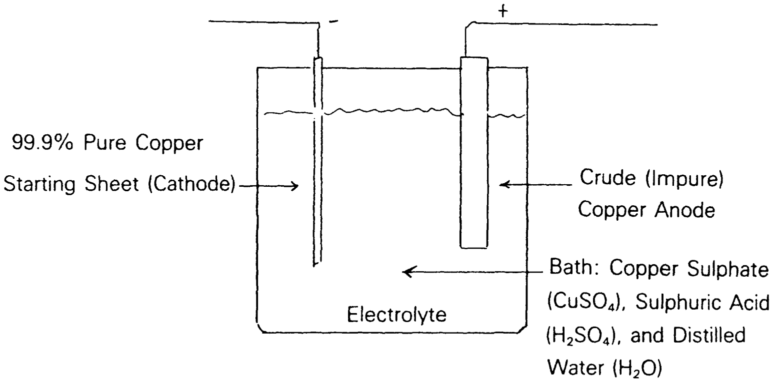


Figure 7.1. Basic copper electrorefining cell

bottom of the cell, in the form of a sludge or slime, as the surrounding copper ionizes. The sludge consists of gold, silver, lead, some copper, selenium, and other metallic elements. See Figure 7.2.

The butt left over from the crude anode is recycled, by melting, into the next anode casting. The sludge is collected and washed free of any soluble salts and then dried and roasted at about 700°F to drive off anything that will become gaseous (volatilize) at that temperature. It is then leached in dilute sulphuric acid to remove any copper and then melted; the selenium and tellurium are removed by fluxing.

The metal that remains after the melt flux operation is now cast into anodes called silver doré anodes. Divided into thousandths, they usually run about 980 parts silver, 15 parts gold, and the remaining 5 parts platinum-group metals and some odds and ends. See Figure 7.3.

When the bath becomes so foul that it is inoperative, the leach acid is added, and the solution is checked for values. You can cement out the metallics with zinc. Wash these and melt them into the crude copper anodes.

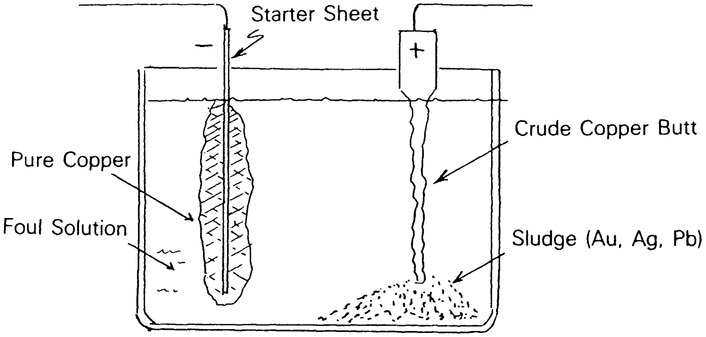


Figure 7.2. End products of copper electrorefining cell

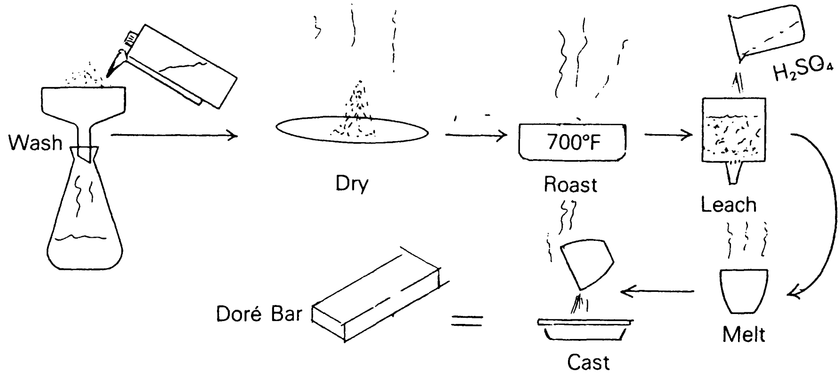


Figure 7.3. Basic treatment of sludge from copper electrorefining cell

The process described above constitutes a parting operation, like the copper, gold, and silver propositions you did with nitric acid, except that done by an electrolytic process.

Electrolytic Silver Refining

Now you are ready to refine the silver doré anode, which was a product of the mud (slimes) from your copper refining. During the melting and fluxing operation and the casting of the crude silver anodes, you can add any secondary silver that you have on hand, such as old jewelry, coins, and photographic wastes.

The procedure is basically the same for silver as for copper, only the crude silver anodes are smaller and are encased in cloth bags to catch the gold and platinum sludge. The electrolyte in this case is a silver nitrate solution with an excess of nitric acid (free acid). The electrolyte is made from silver nitrate salt ($AgNO_3$) which is 63.5% silver by weight, distilled water, and nitric acid.

A typical silver-refining acid bath would be 200 g/L of silver nitrate and 30 g/L of nitric acid.

In this example, a pure silver starting sheet is used for the cathode. See Figure 7.4. In many cases, however, the cathode is made of insoluble stainless steel; coarse silver crystals build up on this type of cathode and are scraped or knocked loose from time to time either manually or by automatic scrapers. See Figure 7.5.

When the crude silver anode is digested, you now have the butt and the slimes in the cloth bag. See Figure 7.6. The butt is then remelted with new crude silver anodes.

The solid silver cathode and the silver crystals are usually 99.9% pure in fineness, requiring only washing. Silver can be sold at this stage as fine silver or can be used to fabricate alloys by various means.

The slime (mud) from the silver cell is washed with lots of hot water, and

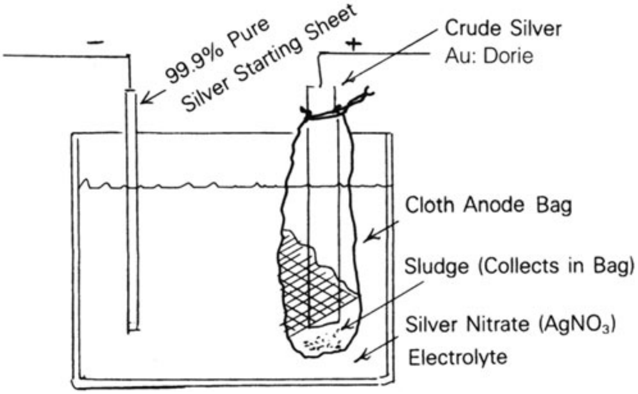


Figure 7.4. Basic silver electrorefining cell

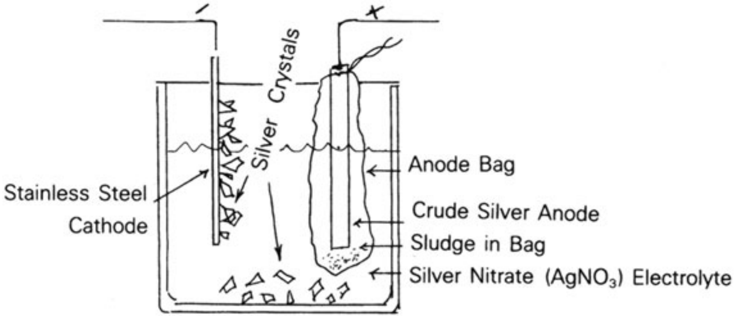


Figure 7.5. Silver electrorefining cell with stainless steel cathode

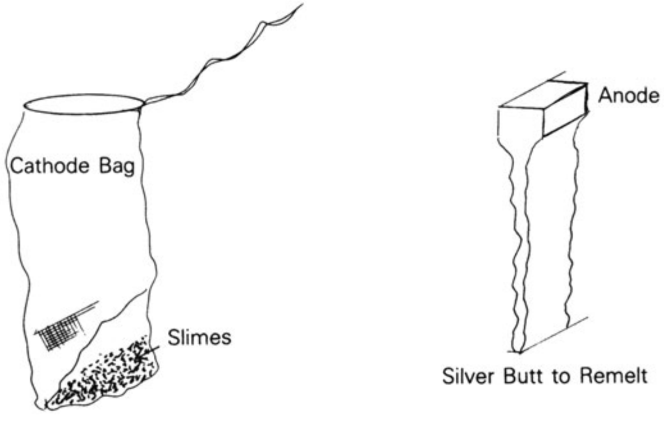


Figure 7.6. Silver butt and slimes

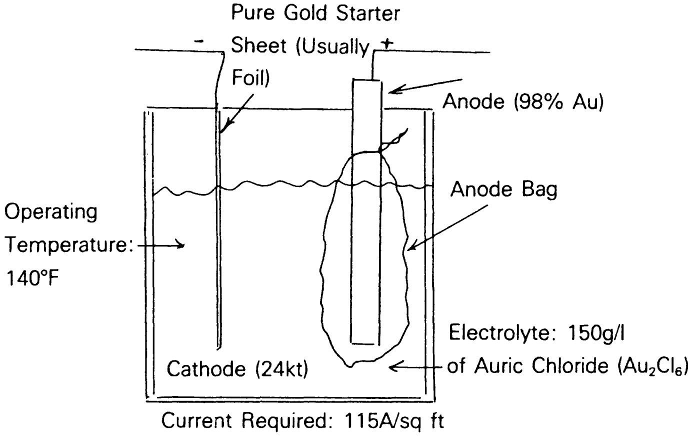


Figure 7.7. Basic gold electrorefining cell (Wohlwill cell)

then with a dilute sulphuric acid wash; it is then melted and cast into crude gold anodes for the gold cell. If, however, the crude silver anode contained only gold and copper, with no platinum group metals, the sludge would only require boiling in sulphuric acid, washing, and melting to become fine enough gold for sale or use.

Electrolytic Gold Refining

The crude gold anode is refined just as the silver was, but with a pure gold starter sheet as the cathode and with an electrolyte made up of a gold salt (gold chloride—$AuCl_3$), distilled water, and hydrochloric acid as free acid. By weight, gold chloride has approximately a 58% gold content. See Figure 7.7.

At the end point, you have 99.9% pure gold at the cathode. The slime consists of such material as silver chloride and osmium; the fouled electrolyte contains platinum, some gold, and copper. See Figure 7.8.

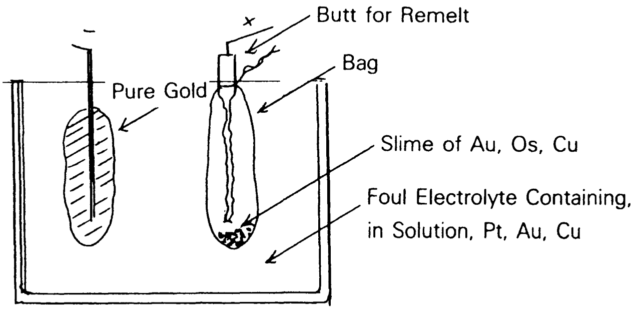


Figure 7.8. End products of Wohlwill cell

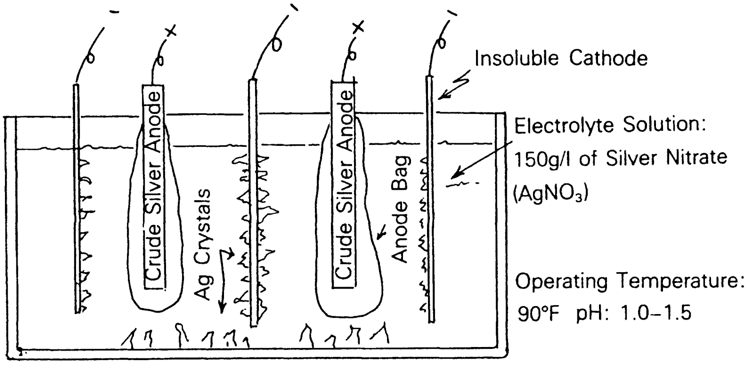


Figure 7.9. Basic Moebius-type electrorefining cell for silver

The electrolyte is stripped of values by cementation. The values are recovered by wet chemical means, as are the slimes.

Types of Cells

The two most common silver cells in use for electrorefining silver are the Moebius cell, in which the crude anodes and the cathode are positioned vertically (see Figure 7.9), and the Thum cell (often called the Balbach–Thum cell), in which the crude anodes are positioned horizontally in cloth-lined perforated frames or baskets made of wood or plastic and in which the cathode consists of a piece of flat graphite on the bottom of the cell. The silver crystals form on, but do not attach to, the graphite cathode. See Figure 7.10.

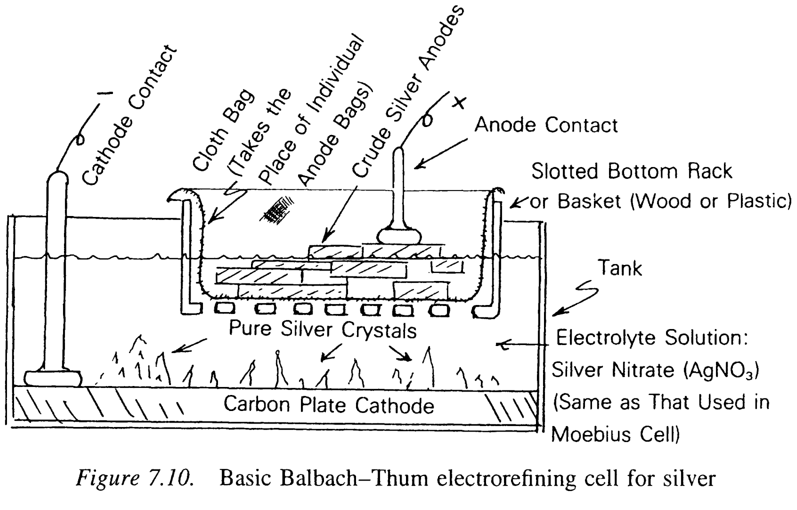


Figure 7.10. Basic Balbach–Thum electrorefining cell for silver

The crude gold anodes are not refined in Thum cells, but in small cells virtually identical to the Moebius cell but called Wohlwill cells. The process of electrorefiing gold was developed by Dr. Emil Wohlwill in 1878, thus the name of the gold cell. The crude gold anode is bagged. The cathode is either a pure gold starter sheet or an insoluble cathode. Titanium cathodes are becoming popular because of their inertness in the electrolyte. The cells are usually no more than a foot square.

In the gold cell, because the electrolyte consists more or less of aqua regia, metals of the platinum group are usually mostly in solution and can be recovered with ammonium chloride and sodium chlorate.

Selecting the Right Cell

The choice of which cell to use and in what combination depends on a lot of factors, such as the in-feed of materials and the relative applicability of the various processes.

Because electrorefining is basically a refining process, you should usually try to have as high a purity on the crude anodes as possible. There are, of course, some exceptions. If you had a copper ore that was primarily copper sulphide, it might pay to extract the metallics by percolating a dilute sulphuric acid (H_2SO_4) solution through the processed (concentrated) ore, and then use this solution, with adjustments, as the electrolyte, from which you could plate out crude copper anodes. These anodes would be impure and would require further processing; the slimes would also have to be processed.

If you are handling material that is largely copper and a base metal, with some gold values—cheap plated ware, electronic pins, circuits—you might elect to simply incinerate, melt, and go with a copper cell and a gold cell (for the refining of the copper cell slimes if they are mostly gold and platinum with minor amounts of silver). The first cell is a copper proposition with a sulphuric acid and copper salt electrolyte; the second cell is a Wohlwill cell with a hydrochloric acid and gold salt electrolyte.

If the material is all high-grade silver and gold, with little base metal, you might elect to add enough pure silver to the melt to cast 90% pure crude silver anodes, making the operation a silver proposition in a Moebius or Thum cell. You could then use a Wohlwill gold cell to handle the slimes from the silver cell.

If the materials you have or handle are mostly platinum and palladium with little gold, then your best bet is to use wet chemical methods, the basic acid process. This would involve separating the little gold with copperas, the platinum with ammonium chloride, and the palladium with sodium chlorate.

Moebius or Thum?

In a Moebius cell, the silver crystals attach to the cathode and must be removed manually or mechanically; the cathode must be cast, drilled, and bolted to the hanger bar. See Figure 7.11. Each anode must have its own bag. The remelt butts are heavier than in a Thum cell and require more silver (remelt) to be in the system at all times; with the Moebius cell, you can have as much as 25% (by weight) of the silver that is being processed locked up in the system at all times. The slimes are relatively difficult to remove and handle.

Because the spacing between the anodes and the cathode is closer in the Moebius cell than in a Thum cell, a lower cell voltage is needed—a savings in power consumption.

Although the Thum cell has its problems, it gets my vote for its ease of operation. You can process small pieces and odd lots, and you can put small, medium, and large anodes together without the bother of bolting and bagging each anode and trying to find a space to hang each in the cell. See Figure 7.12.

Regardless of the method you choose and whether the cell you use is a commercial one or one you have built yourself, you will be faced with systemic problems and limitations and will have to make various compromises.

As I stated before, concentration polarization (too many ions in solution) is usually caused by operating a cell at too high a current density (measured in amperes), resulting in poor-quality cathode plates or crystals.

With both vertical (Moebius) and horizontal (Thum) designs, the rate of ionic production depends on the following factors: the surface area of the cathode, the distance between the cathode and the anodes, the current density, and the composition of the electrolyte (acidity, ionic concentration, impurities, temperature, and so on).

The current density, composition of the electrolyte, and percentage of free acid have the greatest effect on the performance of the cell.

If you have a considerable quantity of platinum-group metals in the crude

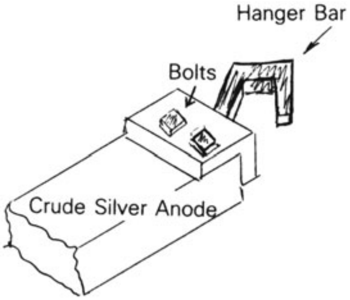


Figure 7.11. Hanger bars required for anodes in Moebius cell

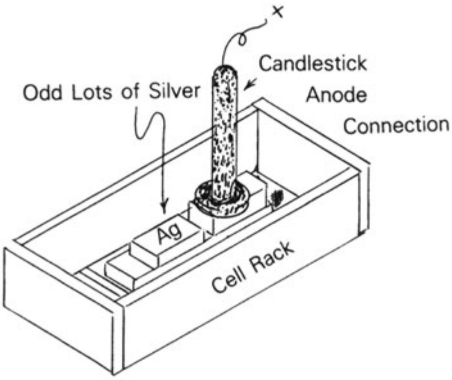


Figure 7.12. Handling odd lots in the Thum cell

anode, it becomes important that fewer of these metals go into solution in a Thum cell than in a Moebius cell, because the Thum cell operates at a lower current density and does not involve mechanical agitation.

Small-Scale Systems

It is possible to run a successful electrorefining operation on a reasonably small scale, but you must remember that you need other equipment than just the cell or cells—a furnace to melt and cast the anodes, chemical extraction equipment to handle the slimes, and so forth. There are advertisements for small-scale electrowinning setups that imply that with this equipment alone you will be able to produce commercially valuable metals with little or no effort on your part. Although these ads do not actually lie to you, they tell a misleadingly incomplete story. The equipment they offer is very much overpriced, too—some as much as 300–400%.

Some equipment advertised as electrowinning or electrorefining setups are actually electroplating setups. Quite a few companies will also sell you cyanide electrolytes to do the refining, although this type of electrolyte is only capable of producing a raw crude impure cathode from a raw crude impure anode, no matter how many times you run the operation. This goes for electrostripping as well as for electrorefining in cyanide solutions.

In the electrorefining examples given previously, the only reason copper sulphate solution is used for copper, copper nitrate solution for silver, and gold chloride solution for gold is that each provides for selective ion transfer through the electrolyte and (as a result) for selective reduction. Cyanide solutions are far better than acid solutions for plating, and 90% of all electroplating baths are cyanide baths using solutions of copper cyanide ($CuCN$), gold cyanide ($AuCN$), or double salts [$K_2Cu(CN)_3$ and $KAu(CN)_2$].

Electrorefining is not an extraction process but an upgrading process in which a nearly pure anode is parted electrochemically to produce an even purer product. As long as your crude anodes are of high enough quality and as long as you are sure that the operation should be handled as a copper, silver, or gold proposition, you should have few problems. Do not hesitate to upgrade an anode by adding high-grade gold or silver to it in order to make the operation a paying proposition. Keep in mind, though, that there is always a point of diminishing returns.

If you have an anode that is say 50% copper and 50% silver, should you melt it with enough copper to come up with a 96% pure copper anode when you recast, and then refine the copper in a copper cell and recover the silver in the slime or sludge? Or, should you add silver to bring the anode up to 98% silver and then refine the silver? Or, should you part the 50% silver and 50% copper bar chemically with nitric acid and recover the silver as a chloride, and then cement and cast the material into a crude silver anode for final purification in a silver cell? Or, should you simply hold the anode aside until you have enough high-grade silver to upgrade it to a crude silver level? The best choice for you from among these various options must be based on all the factors in your own particular situation.

Obtaining Salts for Electrolytes

Copper sulphate is cheap to buy; even though the commercial seller is out to make a profit, if he is a large-scale manufacturer of the salt, he is probably in a position to make and sell the salt to you cheaper than you could make it yourself. On the other hand, making the salt is simple, and you could hold out enough refined copper to produce your own. All that is necessary is to dissolve pure copper in a sulphuric acid solution, dilute it, and evaporate it to crystallization.

If you evaporate a solution of copper sulphate, or silver nitrate, or gold chloride (or any other salt), the solution becomes saturated at a given temperature. A solution is said to be saturated when it will no longer dissolve additional solids and when it remains unchanged in concentration in contact with new additions. The amount of a given solid, by weight, that will completely saturate a definite quantity of a liquid at a given temperature provides the standard expression of the solubility of the substance at that temperature.

If you evaporate the solution past the solubility point of the substance (salt), it will drop the excess substance as crystals (solids). Solubility decreases (and the saturation point lowers) as the temperature of the solvent is reduced. It is very difficult to dissolve a teaspoon of sugar or salt in a gallon of very cold water, but in hot water you can get an enormous amount of either one to go into solution. This is also true of acid solvents, which is why you were directed to use cold aqua regia during your treatment of platinum granules that you did not want to dissolve in the aqua regia.

Therefore, if you concentrate a salt solution by evaporation and then lower its temperature, you will precipitate the solute as crystals. Metallic salt crystals can be purified by simply being redissolved in distilled or deionized water and then recrystallized, one or more times. This system of purification is called purification by recrystallization. The difference between CP reagent grade, technical grade, and commercial grade salts is usually based on how many recrystallizations of the salts have been performed.

When you saturate a solvent at a given temperature and then lower the temperature, and yet no crystallization takes place, you have a condition called supersaturation. This can happen if the vessel used is perfectly smooth and the solution is not disturbed in any way.

The condition of supersaturation is so far from the equilibrium of the saturation at the higher temperature that it is very unstable. You can start the process of crystallization by simply shaking the solution. The usual method of starting a crystallization reaction is by seeding: add a crystal of the material that is in solution to the cooled solution, and the solution will rain crystals until the supersaturated condition of the solution is negated and the solution reaches its proper saturation point for the lower temperature.

The Value of Salts

Most small-scale precious metal refiners see pure metal as the sole goal or end product; however, there is a market for metallic salts for plating baths, reagents, medical and pharmaceutical products, and in industry. An example is silver nitrate ($AgNO_3$).

To make silver nitrate, dissolve pure silver in dilute nitric acid and evaporate all the liquid. Heat the residue to dull redness to decompose any copper nitrate (which could come from either the silver or the nitric acid or both). Redissolve the heated residue in deionized water and crystallize it. Repeat the recrystallization, if it is desirable.

Silver nitrate is called luna salt and is melted and cast into sticks or is sold as is. Some uses of silver nitrate are in photography, in artificial mother-of-pearl, as a reagent, in plating baths, in indelible ink, in glass manufacture, for silvering mirrors, and as a germicide (wall spray). Weak solutions are used in hair dying, to cauterize wounds (styptic stick), in ceramics, and for other purposes.

If you compare the prices of pure silver on the one hand and silver salts and standard silver solutions on the other, you will find vast (and surprising) differences. In some cases, silver nitrate ($AgNO_3$) will be priced at three or four times the spot price of silver, gram for gram. When you consider that silver nitrate is only 63.5% silver by weight, it becomes even more attractive.

The compounds and salts of all metals, precious or otherwise, are part of the refining picture and must be considered not only in terms of their chemical reaction processes but also in terms of their commercial values and uses.

8

Collectors and Separators

Extracting and refining consist of applying various means to collect values and then separating the values from the collectors, singly or in multiples, using various partings and new collectors. The key is to know the solvents and precipitants for each element with which you are working.

If you had a bullion metal that was composed of various elements in combination (an alloy), or if the various elements—say, gold, silver, palladium, platinum, iridium, ruthenium, and rhodium—were a mechanical mixture of finely divided particles, and you dissolved this alloy or mix in aqua regia, the platinum, palladium, and gold would go into solution while the other metals would remain behind as a residue on the filter in the form of iridium, ruthenium, rhodium, and silver chloride (AgCl). In this case, the collector and the separator are selective aqua regia, which performs two functions: collecting the platinum, palladium, and gold, and not collecting the remaining metals.

Next, you separate the platinum, palladium, and gold by selective separation from the common collector. The gold is precipitated with copperas or sulphur dioxide, the platinum with ammonium chloride, and the palladium with sodium chlorate. The platinum and palladium, both of which are precipitated from the collector as chlorides, can then be separated from the chlorine using heat as the separator.

On the other side, you remove the silver chloride from the undissolved metals with another collector—lead, cyanide, or ammonium hydroxide. If you were to choose lead, you would fuse (smelt) the iridium, ruthenium, rhodium, and silver chloride with the lead and then extract or separate the silver, using nitric acid as the collector. This would leave you with a solution containing silver and lead ions. By using a chloride to separate the silver and lead from the nitric solution collector, you wind up with a mix of lead chloride ($PbCl_2$) and silver chloride (AgCl), requiring another separation.

Meantime, the iridium, ruthenium, and rhodium remain combined. Consider iridium first: It is insoluble in single acids, in water, and in alcohol; it is slightly soluble in aqua regia; and it is soluble in fused alkalies. Next, consider ruthenium: It is not soluble at all in aqua regia, water, single acids, or alcohol but (like iridium) is soluble in fused alkalies. Last, consider rhodium: It seems to be soluble only in fused potassium bisulphate or sodium bisulphate, which are themselves water soluble.

If you fuse the iridium, ruthenium, and rhodium, using potassium or sodium bisulphate as the rhodium collector, and then dissolve your fusion in water, the rhodium ions will be left dissociated in water, and the iridium and ruthenium will be left as a residue on the filter. In this case, the sodium or potassium bisulphate is the collector of the rhodium.

I will take you through a separation of the complete set of the metals iridium, ruthenium, rhodium, osmium, silver, platinum, palladium, and gold, step by step, later in this book. The partial explanation I just gave is simply to illustrate the importance of knowing the solvents and precipitants (and by-products) of the metals at hand. Whenever you can concentrate the values you are after—whether by sluicing, panning, flotation, wet chemicals, heat, or smelting—in such a way as to get rid of as much of the unwanted material as possible, it makes the remaining task of collection and separation simpler and cheaper.

Imagine that you have a huge pile of electronic scrap, which, after close visual examination and some assay work, you determine consists mostly of base metals, plastic, Bakelite, and paper, with the precious metal values—some exposed and some unexposed (encapsulated)—in the form of single-layer platings of precious metal (gold, silver, and so on). Now, imagine that you have an ore that is carrying approximately 2 ounces of silver per ton and perhaps 1 ounce of gold per ton, according to your assay.

In both cases, you are faced with a problem. You simply cannot boil a ton of ore or a ton of electronic junk in acid, even if the acid cost two cents a pound. The electronic scrap or ore must be broken up, crushed, and ground in order to expose and release the values, so that you can get at it with whatever collector you choose. The electronic scrap must then be incinerated to remove burnables, whereas the ore must be roasted to rid it of sulphides, arsinides, zinc oxides, and organics.

You might next concentrate the values of your ore by washing, tabling, and so on. This you would definitely do with your electronic scrap. The purpose in each case is to upgrade the material—that is, to raise the percent weight of the values against the total weight of the retained material.

At this point, you might decide, based on what the final upgraded material looks like and what the assay shows, to leach both the ore and the electronic scrap with a dilute cyanide solution in order to collect the values, and then precipitate the values using zinc ion exchange, or a cyanide stripping cell and steel wool, or activated carbon, or chlorine.

In each case (electronic scrap and ore), much of the equipment used is the same or very similar. If you had high-grade gold or silver scrap, you would add gold or silver to upgrade the anode and refine with an electrolytic cell, or use wet chemical methods.

Collectors

Solutions

Solutions are the primary collectors used in refining. A solution is a homogeneous mixture of two or more substances that undergo no separation upon standing. The term "solutions" includes not only mixtures that are liquid at room temperature but also those that are liquid only at other particular temperatures. Molten lead, for example, can be used as a solvent solution.

Elements that are soluble in the same solvent can be separated by adding another solvent, in which one or more of the elements in solution is more soluble than the other(s), to the first solvent. This is called extraction by the partition principle.

"Miscible" means capable of being mixed to form a homogeneous substance (usually referring to liquids); "immiscible" means the opposite (also referring to liquids). When a pair of solutions, or a solvent and an element, are able to form solutions in any proportion, as alcohol and water are, they are said to be miscible in all proportions.

The partition principle is based on the fact that many solutes are soluble in liquids that are practically immiscible. For example, iodine is 675 times more soluble in carbon disulphate than it is in water, and carbon disulphate is practically immiscible with water. If you add to a solution of iodine in water, a small volume of carbon disulphate solution in a separatory funnel and then shake them together well, the carbon disulphate, because of its affinity with the iodine, will pick up the iodine from the water; then, as it is immiscible with water, it will separate, leaving the water free of iodine. See Figure 8.1.

This process of shifting a solute from a solvent in which it is less soluble into one in which it is more soluble is called extraction. It can be a very useful tool in many types of analysis and assaying and in various industrial manufacturing processes.

A similar case of the partition principle involves the use of lead as the collector. Silver, platinum, palladium, copper, and rhodium (among other metals) are readily soluble in molten lead but are much more soluble in molten zinc; and, as zinc is practically insoluble in molten lead, you have the very same set of conditions that you had with the iodine, water, and carbon disulphate proposition.

Lead

In lead smelting and refining operations, the precious metal values are primary precious metals from the lead ore. The lead is melted in large cast-iron kettles;

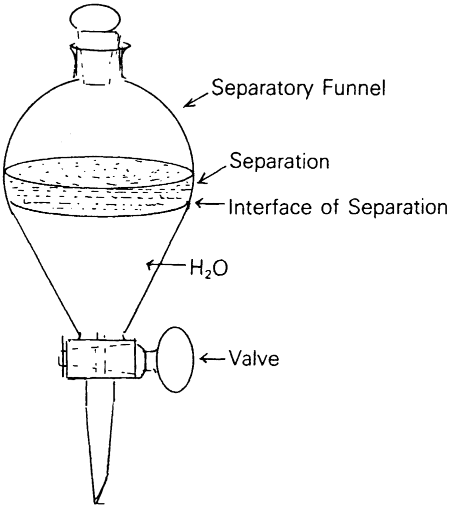


Figure 8.1. Separation using the separatory funnel

molten zinc is then poured into the liquid lead and rabbled (stirred) into the lead, where it combines with the precious metals, floats up to the top and is skimmed off as a zinc–lead dross. This is known as the Parks process. The precious metals are separated by conventional methods—such as removing the zinc by distillation and the lead by cupellation or by wet acid methods—and then parted and refined as usual.

A reverse Parks process can be undertaken, using lead as a collector. Add crushed ore or ground black sands to molten lead, rabble them in, skim off the gangue (mostly sand quartz), add molten zinc, and collect the values. This is called a lead scorification.

In a fire assay, lead is used to collect the precious metal values in an ore in order to determine the value of the ore (expressed in ounces per ton).

A weighed sample of the ore in question is crushed and roasted to a dull heat to expel the sulphides. The ore is mixed with a flux containing litharge (lead oxide—PbO). Litharge is the basic flux component and the source of lead to do the collecting. The mixture of ore and litharge is placed in an assay crucible.

The crucible is heated in the assay furnace, which reduces the litharge to lead and liquifies the charge. The process (and its product) is called fusion. The fusion is poured into a cast-iron mold, where it forms a lead button. The lead button is placed in a cupel—a cylindrical block (usually made of bone ash) with a shallow cup on top—and the cupel is heated in an oxidizing atmosphere with the draft open or the door cocked.

In the assay furnace, the lead and the oxidizable metals are reduced to oxides (lead to litharge, copper to cuprous oxide, and so on), and these oxides are absorbed by the cupel, leaving behind a precious metal bead that is weighed and parted chemically to determine the precious metal values. Often, inquarts of pure silver are added to the crucible fusion to ensure a good parting in an assay for gold and silver. Enough pure silver is added to lower the proportion of gold in the gold–silver bead to 6kt or lower. The inquarts (which you buy) come with an assayed weight, which is deducted from your results, based on the assay of the inquarts and the total weight used.

Other Elements and Compounds

Gold, silver, and many base metals will mix with mercury. Platinum-group metals will not. The old saying is that everything floats on mercury but gold, which it swallows. Mercury, when clean, will mix at room temperature with the values to form what is called a mercury amalgam. The gold prospector uses a little mercury in his pan to collect very fine values or has a separate small copper pan for the same purpose.

When gold and silver are leached with dilute, alkaline cyanide solutions and oxygen, they form cyanide complexes. The chemical equation for a typical gold–cyanide chemical reaction is $4Au + 8KCN + O_2 + 2H_2O \rightarrow 4KAu(CN)_2 + 4KOH$. The oxygen ($O_2$) in the above reaction comes from the air.

Chlorine is a diatomic gas that is heavy, noncombustible, greenish yellow, pungent, corrosive, and suffocating. The main method of manufacturing it is by the electrolysis of sodium chloride (table salt). Chlorine is a very strong oxidizing agent and will form chloride compounds with many elements.

There are various systems using chlorine gas and chloride compounds to collect values. A simple device using chlorine gas to collect values (in the form of chlorides) from ores in order to assay the value of the ores is shown in Figure 8.2.

You have a choice of generating your own chlorine gas, as in Figure 8.2, or using a lecture cylinder of chlorine. The gas washing bottle should have a medium-sized fritted filter.

To operate the setup shown in Figure 8.2, take about 200 g of the ore in question, spread it out, and roast it at a dull red heat until you can smell no more sulphur odor. Then rub the assay well in an iron mortar, and repeat the roasting treatment. The roasting can be done in a dry steel gold pan that has been painted with a thin coat of a mixture of kaolin clay and just a little water. When the assay is cool, place it in a clean porcelain evaporating dish, and go over it with a magnet to remove any iron; then moisten the assay with just enough water to make it damp but still loose and porous.

In order to get a perfect gold extraction, three conditions must exist. First, the assay to be treated with chlorine must be free of metallic iron. Second, the roasting must be carried out very carefully so that there are no undecomposed metallic sulphides and arsenides. Third, the chlorine gas must be free from hydrochloric acid, which not only would dissolve all metallic oxides present but

Some Common Metallic Chloride Compounds

Aluminum Chloride	$Alcl_3{\cdot}6H_2O$
Anhydrous Aluminum Chloride	$AlCl_3$
Cadmium Chloride	$2CdCl_2{\cdot}5H_2O$
Coblat Chloride	$CoCl{\cdot}6H_2O$
Cupric (Copper) Chloride	$CuCl_2{\cdot}2H_2O$
Ferric (Iron) Chloride	$FeCl_3{\cdot}6H_2O$
Indium Chloride	$InCl_3$
Nickel Chloride	$NiCl_2{\cdot}6H_2O$
Palladium Chloride	$PdCl_2$
Platinum Chloride	$PtCl_4{\cdot}5H_2O$
Rhodium Chloride	$RhCl_3{\cdot}3H_2O$
Silver Chloride	$AgCl$
Stannous (Tin) Chloride	$SnCl_2{\cdot}2H_2O$
Zinc Chloride	$ZnCl_2$

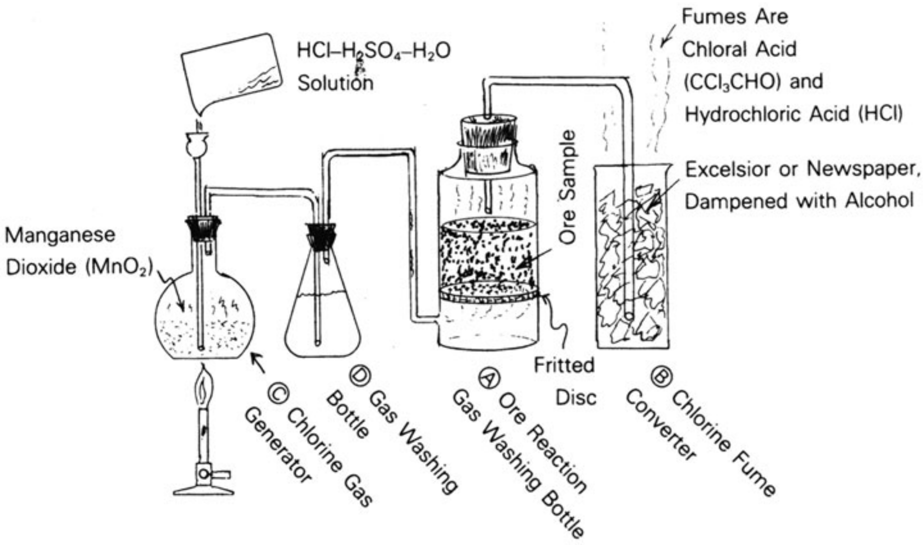


Figure 8.2. Simple assay system using chlorine gas

also—in the presence of iron sulphides—would evolve hydrogen sulphide, which, in turn, would decompose the gold chloride, precipitating the gold as gold sulphide. Hydrogen sulphide would also absorb the chlorine, so that the extraction will be minor.

When the three conditions above are (as nearly as possible) present, you can go on with the process. The damp assay is placed in the gas washing bottle as loosely as possible on the fritted disk. A tube is then run from the gas washing bottle down into the beaker, which is filled with loose wood chips, excelsior, or small loosely rolled-up pieces of newspaper. See Figure 8.3.

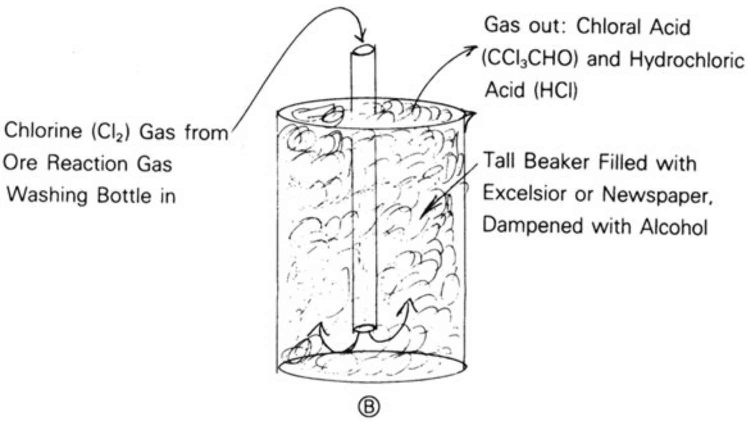


Figure 8.3. Chlorine fume converter

The wash bottle "D" in Figure 8.2 is filled with distilled water. Washing the assay with this water will strip the chlorine of hydrochloric acid, so that clean chlorine gas will go to the gas wash bottle containing the assay.

The amount of chlorine gas needed to assay 200 g of material can be generated using the following recipe. Place 10 g of manganese dioxide in the generating flask. Mix together 10 g of hydrochloric acid and 10 g of sulphuric acid, and dilute this with an equal volume of water. Add this acid mix to the manganese dioxide, and heat the generator, lightly at first, but then a little more strongly when gas starts to generate. The gas will begin to change all the finely divided gold into gold chloride as soon as you see gas in the top of the gas wash bottle containing the assay. It will take about an hour of gassing the assay to ensure that all the gold is converted.

Just before starting the chlorine generation, moisten the material in the tall beaker with alcohol. This will cause the exhausted chlorine gas from the assay gassing bottle to be converted to chloral (CCl_3CHO) and hydrochloric acid (much less offensive than chlorine gas) when it comes in contact with the alcohol on the excelsior or chips.

The instant you stop heating the generator, be sure to disconnect the first wash bottle from the generator. If you fail to do this, the vacuum formed in the generator as it cools will suck the water that is in the wash bottle into the generator, which will explode.

The contents of the gas wash bottle containing the assay are washed into the filter funnel and there washed well with very dilute hydrochloric acid. The solution is gold chloride. Add some full-strength hydrochloric acid to it and warm it up. You can then precipitate the gold with copperas, sulphur dioxide, oxalic acid, or whatever reagent you choose.

The gold powder is then boiled in sulphuric acid, washed free of acid, dried, and weighed. You can do two things to check for silver content. You can dry the residue on the filter, wrap it in test lead foil, and fuse it. (Test lead is a purchased, almost pure lead that comes with a batch assay for correcting your results.) This will pick up any silver that was in the form of insoluble silver chloride produced by the chlorine gassing operation. Then, cupel the lead and weigh the silver bead if any; or you can mix the residue from the filter with ammonium hydroxide to put the silver chloride into solution. Filter and precipitate the silver chloride by acidifying the ammonium hydroxide with nitric acid, and take it from there.

Bromine is a reddish brown, nonmetallic halogen. A halogen is one of the electronegative elements in group VIIA of the periodic chart; the halogens are (in descending order by activeness) fluorine, chlorine, bromine, iodine, and astatine. Fluorine is the most active of all chemical elements.

At normal room temperature, bromine is a liquid. It attacks (corrodes) most metals, including platinum, and palladium. It attacks aluminum violently and potassium explosively. Bromine is derived from seawater and natural brines as a salt, which is then oxidized with chlorine. It has many commercial uses similar to chlorine, such as in bleaching and as a reagent. When bromine is substituted for chlorine as a collector in the vat process or barrel process, the process is called bromination.

You have seen that when a gold–silver alloy or combination is digested in a single acid, such as nitric acid, the silver will be collected as dissociated silver ions in solution, with the gold remaining behind undissolved; you have also seen that a multitude of metallic ions can be collected in a single aqua regia solution (platinum, palladium, gold, copper), whereas other metals (silver, iridium, ruthenium, rhodium, osmium) do not ionize.

Alkaline fusions are also important collectors. In a metallic combination of iridium, ruthenium, rhodium, and osmium, for example, the rhodium can be separated and collected from the other metals by the fusion of the metallic combination with sodium bisulphate.

It is impossible to distinguish completely between collectors and separators because a collection operation can usually be viewed as a separation operation and vice versa. If you have sand mixed with salt and dissolve the salt, using water as your solvent, have you collected the salt in the water, or collected the sand from the salt, or separated salt from sand, or separated sand from salt? It depends on how you look at it.

Separators

Once you have collected some material—solid, gaseous, or liquid—by dissolving it in a solvent (thereby separating it from one or more other materials that the solvent did not affect), you will want to separate it from the solvent or collector. Here, again, you can go in many different directions and still come up with the same end results.

Precipitation Methods

The most common method used to separate a constituent from a solvent or from a combination of elements is to put the entire solvent or combination in a common solvent and then to drop the desired constituent out of the solution as a solid by selective precipitation, adding the appropriate catalyst.

To understand what precipitation is and why it occurs, you must have a good understanding of equilibrium reactions. You may remember my earlier discussion of saturated solutions and supersaturation and the stress required to cause a supersaturated solution to precipitate the excess solute as crystals. The law of mass action, formulated by LeChatelier, states that when a stress is applied to a system in equilibrium, the system changes to a new equilibrium, and this change tends to reduce or relieve the stress applied. A stress can be applied to something that is resting in equilibrium by introducing a change in pressure, in temperature, or in quantity of reactants.

At equilibrium, opposing forces and reactions are equal and cancel out each other. An equilibrium rate of change is zero, and the equation for equilibrium rate is expressed as $\rightarrow \overset{=}{\mathrm{o}} \leftarrow$.

Before you add a precipitant to a solution, you must bring the solution into equilibrium. This will maximize the efficiency of the precipitation reaction. The trick then is to set up the conditions (the applied stress) in such a manner as to cause the precipitation to be as complete as possible. It never is 100% complete, as every precipitate is minutely soluble regardless of its composition.

When platinum is precipitated from a chloride solution with ammonium chloride, for example, the solvent left behind will always show platinum content when spot tested. The amount of platinum in the solvent is very small, though, and of little consequence. The same goes for gold dropped from solution with copperas, sulphur dioxide, or anything else: Some gold is going to stay behind.

Some Precipitants

Hydrogen sulphide, a base, is one of the most frequently used precipitants in solutions whose initial pH is controlled by an acid, such as hydrochloric acid. By altering the pH of a solution, you can separate many of the elements it contains from the others.

Ammonia, a solution of ammonium hydroxide, is also a base and can be used to raise the pH of a solution to the point at which hydroxides of various metals will precipitate; if you are skillful with buffers, you can separate many elements from the others using ammonia. Ammonia will precipitate hydroxides of aluminum, berylium, bismuth, chromium, iron, lead, titanium, and rare-earth metals; in the presence of phosphoric, arsenic, silicic, and hydrofluoric acids, it will precipitate various other substances.

Ammonium carbonate or oxalate will precipitate carbonates of calcium, strontium, and barium from solutions neutralized with ammonia and then made slightly basic with just an excess of ammonia past the solutions' neutral point.

Ammonium sulphide will precipitate sulphides of iron, zinc, manganese, cobalt, and nickel, and hydroxides of aluminum and chromium from neutral or alkaline solutions.

Barium chloride will precipitate barium sulphate ($BaSO_4$) from acid solutions of barium sulphate.

Hydrochloric acid will precipitate silver, lead, and mercury, as silver chloride ($AgCl$), lead chloride ($PbCl_2$), and mercuric chloride ($HgCl_2$), respectively, from nitric acid solutions.

Silver nitrate will precipitate silver chloride, silver bromide, or silver iodide from the corresponding elements in a water solution or nitric acid solution.

Ammonium chloride will precipitate platinum and iridium from an aqua regia solution whose nitric acid has all been expelled (by repeated boiling down).

Sodium chlorate will precipitate palladium from the chloride solution (nitric-acid-free aqua regia) above.

Iron sulphate (copperas) will precipitate gold from nitric-acid-free aqua regia, as will oxalic acid; sulphur dioxide gas will precipitate gold from an acidic aqua regia solution.

In general, the most frequently used inorganic precipitants are common acids and salts. Hydrochloric acid is used to precipitate silica from silicates and to precipitate silver as an insoluble silver chloride; sulphuric acid is used to precipitate barium or lead salts as sulphates.

These are only some of the many reagents used to precipitate elements from solutions. They are, however, the ones that are most important in the recovery of precious metal values.

Coprecipitation takes place when two or more elements are precipitated with a common reagent, as when platinum and iridium both come down from a solution to which ammonium chloride has been added. In this particular case, due to the time delay between the two precipitations, you can effect a separation of the coprecipitates.

A xanthate is a salt of potassium or sodium and xanthic acid. These two xanthates are available in the form of solid, water-soluble pellets. They are classified both as collectors and as separators. They are used in flotation cells in the flotation of various sulphides and metallics, such as copper, silver, and gold.

Volatilization

Separation of silver and gold from mercury in an amalgam of the three elements is the classic example of volatilization. Mercury goes to vapor at 356.6°C, gold goes to vapor at 2808°C, and silver goes to vapor at 2212°C. Heat the amalgam above 356.6°, which reduces the mercury to vapor, and run the vapor off into a condenser, and you have a separation.

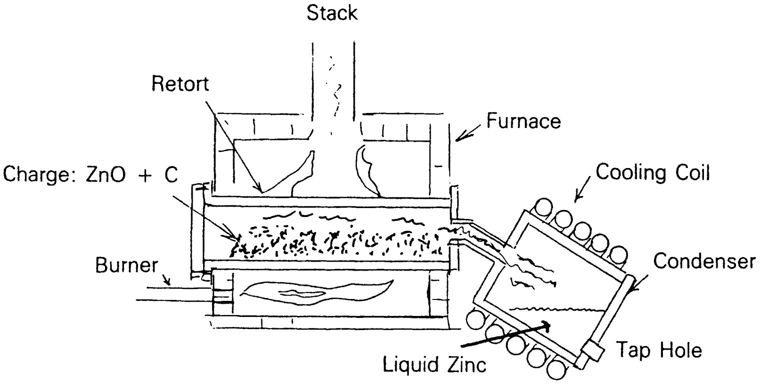


Figure 8.4. Reduction of zinc oxide with carbon

Volatilization is a widely used system of separation for a great many compounds. In a vacuum chamber, you can do unlimited separations. As you lower the pressure, you lower the vaporizing temperature of the element. Zinc and lead can be selectively separated from an alloy (brass) of zinc, lead, and copper by this method.

The extraction of zinc in the form of flotation concentrations of zinc sulphide is based on the fact that zinc boils at 907°C. The concentrate is roasted to drive the sulphides off, converting the zinc sulphide into zinc oxide. Next, the zinc oxide is mixed with carbon (charcoal) and heated to the point needed for the reduction to pure zinc and carbon monoxide: $2ZnO + C_2 + \text{heat} = Zn_2 + 2CO$. The reduction with carbon is done at a high temperature to limit the carbon dioxide (CO_2) content in the retort, to prevent the zinc from oxidizing. The reduced zinc is a vapor; it is condensed to liquid zinc in a water-cooled condenser. See Figure 8.4.

Electrolytic separation is done in Wohlwill, Moebius, Balbach–Thum, and steel wool cells. Electrolytic separation is sometimes called a precipitation, but it is not a true precipitation because the metallic ions being drawn out of solution by the electromotive force of the cell are not being replaced by other ions, as they would be in a true precipitation.

Pregnant cyanide solutions can be stripped by percolating them through activated charcoal, which will extract the values. The charcoal is then stripped (another separation) by volatilization—either by burning the charcoal to ash and then recovering the metallic values or by stripping the charcoal with a hot caustic soda solution (sodium hydroxide).

Ion Exchange

Ions can be precipitated from solution as metallic values by exchanging their place in a solution with ions of a less noble metal.

Recently, ion-exchange resins have been used with increasing success to separate precious metal values from solutions. Ion-exchange resins are synthetic resins containing active groups that give the resins the property of exchanging ions between themselves and a solution. Some of the active groups used in these resins are sulphonic, carboxylic, and phenol groups.

The sulphonic group consists of organic acid compounds containing the sulphonic acid group (SO_2OH). The carboxylic group ($COOH$) is the group characteristic of organic carboxylic acids. The phenol group (C_6H_5OH) is the carbolic acid group.

Some ion-exchange resins are activated with the univalent amino group (NH_2). This amino acid group is quite extensive; it includes glycine, alanine, phenylalanine, tyrosine, valine, leucine, isoleucine, serine, threonine, cysteine, cystine, methionine, asparagine, glutamine, lysine, arginine, aspartic acid, glutamic acid, histidine, tryptophan, and proline.

Ion-exchange resins have hundreds of uses, from softening water and milk to increasing the effectiveness of cigarette filters. In milk softening, the resin exchanges sodium ions for naturally occurring calcium ions. Manufacturers have put miniature ion-exchange resin units in some cigarette filters to remove radioactive polonium (Po) from the smoke.

Other Separators

Zeolite is a natural ion exchanger—a hydrated silicate of calcium and aluminum.

A chelate is a type of coordination compound—a form of complex molecules or ions used in the separation of ions from others by extraction or partition methods.

Finally, there are various types and kinds of stills for separations: distilling the conventional way, distilling in a vacuum, steam stills, and others.

Fractional distillation occurs by separately collecting fractions boiling at different temperatures. Fractional crystallization occurs when you separate a mixture of various substances by making use of their different solubilities. The solution containing the mixture is evaporated until the least soluble compound crystallizes out. These crystals are removed, and the evaporation is continued for the next to least soluble compound, and so on.

9

Wet Chemical Master Plan

Assume that you have refined your material to the stage designated point "x" on the flow chart in Figure 9.1; the material is now in the form of a bar or meltable granules or dust, which can be melted or made into a lead fusion, then cupelled or granulated. The decision as to whether or not to make a lead fusion and cupel depends on the condition of the material. If it carries sufficient copper, lead, and other base metals to require an excessive expenditure of acid to part them, or if it carries gangue such as sandy material, you might elect to fuse the material with lead and cupel it to get a cleaner product that can be handled easier and at less cost.

In a lead fusion, the material is mixed with a stock flux (soda ash, borax, and glass) to which is added litharge (lead oxide—PbO) and fluorspar (calcium fluoride—CaF_2). The material and flux are then melted together; the fluorspar fluxes the sandy gangue by liquifying it, and the litharge is reduced to lead. The oxygen released by the litharge during its reduction furnishes oxygen to burn off the combustible materials. The lead formed from the litharge collects the values and the base metals present, such as copper. The lead is cast into ingots, and the slag from the fusion, which still carries minor amounts of values, is recycled.

The lead is charged (inserted) onto the hearth of the cupel furnace, where it is melted under oxidizing conditions. This process oxidizes the lead back into litharge. The precious metal values—gold, silver, platinum—remain as an alloy while the copper oxides dissolve in the litharge and other unwanted oxides are soaked up by the hearth, which is made of bone ash. The litharge is reused in the next batch. See Figure 9.2.

What you are doing is the same thing you would do in a fire assay, but on a large scale. Lead fusion and cupellation are widely used in the processing of huge lots of sweeps, buffs, and slimes. A ton of sweeps are reduced to a few hundred pounds of collector lead pigs.

If the bullion you produce contains silver above a few percentage points, say

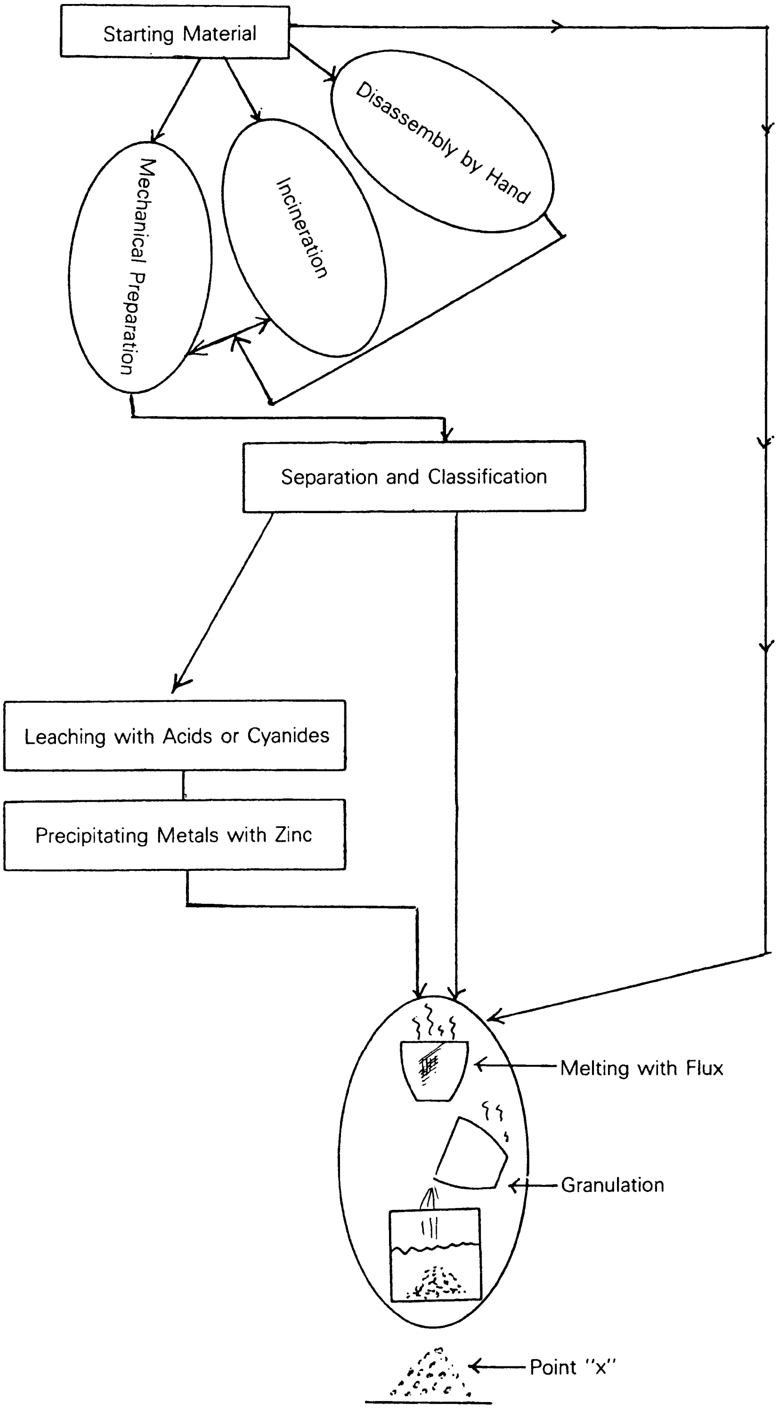


Figure 9.1. Flow chart of master plan to point "x"

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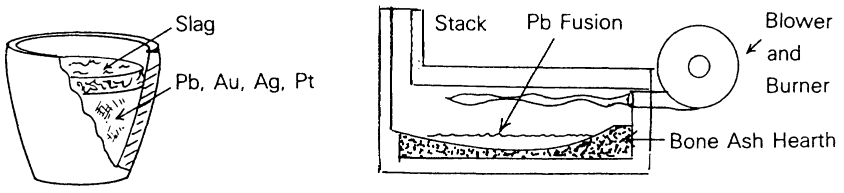


Fusion

Cupellation Furnace

Figure 9.2. Lead fusion and cupellation

10% or more, the bullion should be parted with nitric acid to recover the silver as a nitrate. If it is below 10%, it will be present in the first residues of your refining operations as silver chloride and can be removed at that point with ammonium hydroxide.

Some operators prefer to make a lead fusion of the first residue from the aqua regia digestion and then to extract the silver by dissolving the lead fusion with nitric acid. When you precipitate the silver as a chloride from the silver–lead nitrate solution, you get a mixture of lead and silver chloride. I do not see what has been gained by this extra step.

Step-by-Step Procedure

Melt and pour the material in a thin stream into cold water. Pour when the metal is at 2150°F and has been skimmed free of slag. The slag is easily removed by adding a small amount of dry silica sand to the crucible to coagulate (by chilling) the slag; in this chilled, gummy state it is easily removed by being rolled up on a short length of dry cold-rolled black iron. Pour from a height of 3–4 ft above the water bath, using a circular motion. See Figure 9.3.

At this point, you have granulated bullion. The granulation serves to increase the surface area of the material, giving the acids more surface area to act upon. You are now at point "x."

If you think of the separation process as a trip in a delivery truck, you can imagine dropping off each metallic value at a different destination. Now, if you knew exactly what was in the truck and where each parcel was going, you would plan an efficient delivery route, with no backtracking or detours, and then drop off each at its correct destination in rotation and head home.

Your task is not quite so simple. You could have only two parcels (gold and silver) in the truck or three (gold, copper, and silver) or seven (iridium, ruthenium, rhodium, osmium, silver, platinum, and palladium)—not counting worthless parcels (base metals) and trash (leftover gangue) that just get in the way. Looking in the truck is not going to tell you much. You are going to have to look inside (assay) the truck's parcels to determine what you have. This means making a series of partings, extractions, precipitations, and separations as you go along.

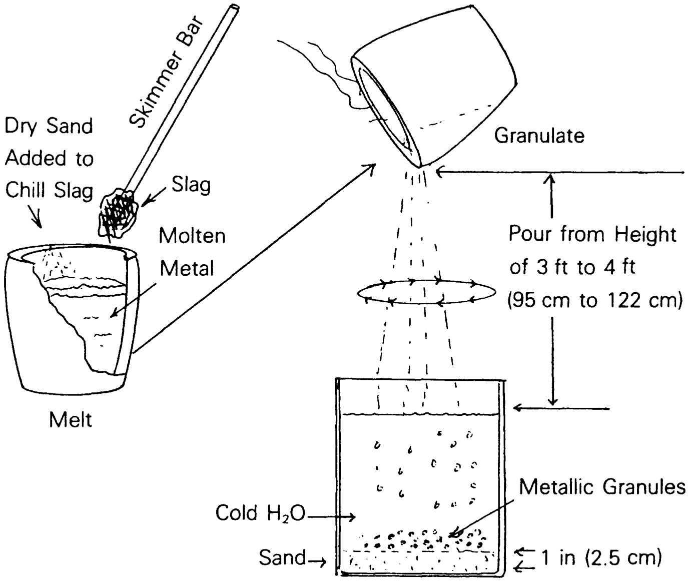


Figure 9.3. Granulation

Each time you locate or separate a particular element, you make your delivery of that one, then sift out the next and deliver it to its destination, until you are unloaded.

Obviously, it would not be too smart to go to all destinations possible when you only have a couple of parcels (values) to deliver. This is where testing comes in—spot testing, blow pipe testing, and so on. After each delivery, you check to see what is left. Your testing ability becomes your X-ray eye.

The various extractions and separations that you will make correspond to delivery stops; the load corresponds to the burden. I call the material obtained at a delivery point the product or end point. The flowchart is the run or road map.

Burden: Silver Chloride

Suppose, for your first run, that you have identified silver chloride as the only value-bearing burden in your material. The object is to make the run in as straight a line as possible, with the product at the end point pure metallic silver of high fineness. See Figure 9.4.

As Figure 9.4 indicates, you can take any of three directions, all of which are quite direct, to reach your end point. The decision is yours, and, like many decisions of this type, your choice will be based on the quantity of material you have, your physical lab setup, and your own personal preference.

Direction 1. In this case, beginning at stop "A," you mix the silver chloride

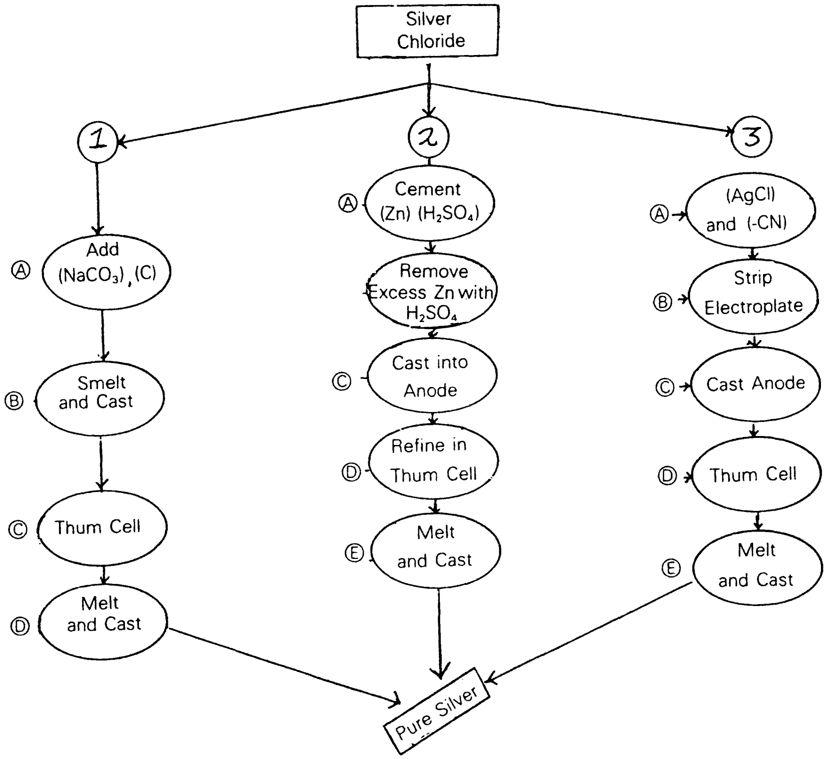


Figure 9.4. Silver chloride flowchart

with a flux of sodium carbonate and charcoal, soda ash, and borax. At the next stop, "B," you melt the mixture of flux and silver chloride, reducing the silver chloride to metallic silver, and then cast this into a silver anode. At stop "C," you refine the silver anode in a Thum cell. The silver crystals from the Thum cell are collected at stop "D," melted with a little borax flux, and cast into a high-purity silver ingot. You are now at the end point.

Direction 2. Beginning at stop "A," you cause the silver chloride to be cemented out as silver by ion exchange with zinc or iron. This involves covering the silver chloride with a solution of 1 part sulphuric acid (H_2SO_4) and 15–20 parts distilled water, and adding mossy zinc or iron nails. The cementation is accomplished when the silver chloride comes into contact with the iron or zinc in the dilute sulphuric acid electrolyte. At stop "B," the cemented silver is relieved of excess zinc with sulphuric acid and then washed. In the case of iron, the iron is simply physically removed. At stop "C," the cemented silver is melted with a simple flux of borax and a pinch of saltpeter, and cast into an impure anode. At stop "D," it is electrorefined in a Thum cell. At stop "E," it is remelted and cast into a pure ingot.

Direction 3. Beginning at stop "A," you dissolve the silver chloride in a dilute solution of sodium cyanide or potassium cyanide. At stop "B," in a plating cell, you strip the silver ions from the cyanide solution onto a pure silver cathode starter sheet, or onto an insoluble stainless steel cathode, or onto steel wool, or you add zinc to the solution and precipitate the silver as metallic silver. Whenever you use zinc to strip a solution of metallic ions, regardless of whether the solution is basic or acidic, you should hang a zinc plate in the solution to prevent the precipitated metal from redissolving. The plate acts as a kind of ion buffer. At stop "C," you cast the nearly pure silver into an anode. At stop "D," you refine the silver in a Thum cell, and at stop "E," you cast it into a pure ingot.

Burden: Silver, Gold, and Mercury Amalgam

See Figure 9.5. Amalgams of gold, silver, and mercury result from extracting free gold and silver values by running the crushed ore across silver-plated copper plates that have a coating of mercury or by running it through a mercury tumbler—the mercury becoming saturated with the fine particles of silver and gold.

Gold and silver are not soluble in mercury, as is stated in most texts (I am guilty myself, by force of habit, of referring to them as being soluble in it). The gold and silver simply combine with mercury to form a pasty mixture. It is analogous to the relationship of diamonds and grease: Diamonds have an affinity for grease and are collected on greased plates. Now, it is obvious that diamonds are not soluble in grease. With mercury, the same thing is happening but not as obviously: The finely divided gold and silver have an affinity for mercury and will sink into it (attach themselves) like flies to flypaper. Still, it is only a mixture—not a compound or solution.

At point "A" of Figure 9.5, the amalgam is subjected to squeezing to remove as much mercury as possible. The old-timers' method was to squeeze the amalgam through a chamois by placing the amalgam in the chamois and twisting it into a ball, tighter and tighter. The mercury would sweat through the chamois, leaving behind the gold, silver, and some mercury. This method is not really a good idea because it puts you in skin contact with the mercury. As innocent as mercury looks, it is very poisonous and can be absorbed through the skin.

The preferred small lot method is to place a wet cotton wad in the bottom of a hypodermic syringe, place the amalgam in the barrel, replace the plunger, and squeeze the amalgam against the wet cotton. The mercury goes through, leaving behind a slug of gold, silver, and some mercury. You will find that this method produces an extremely fine separation, compared to the chamois, and at the same time is much easier.

At point "B," the mostly gold and silver slug is placed in an approved mercury retort and condenser train. The sealed retort is heated to a red heat, vaporizing the mercury. The mercury vapors are carried over to the condenser, which cools the vapor below the vaporizing temperature of mercury, causing the mercury to

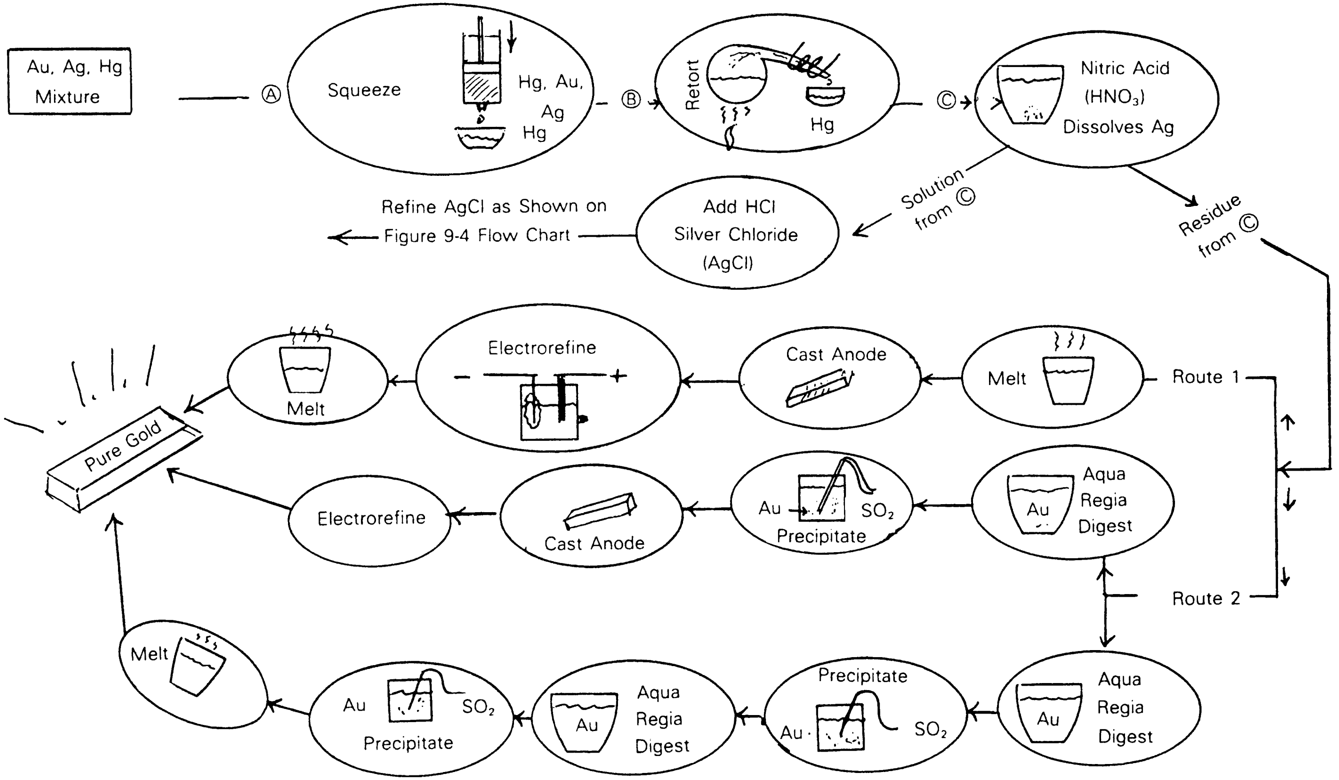


Figure 9.5. Mercury amalgam flowchart

be discharged in liquid form into the mercury recovery dish under a covering solution of 5% nitric acid and 95% water. The residue is removed from the retort as a gold, silver, and mercury residue.

At point "C," the residue from the retort is digested in a 1-to-1 solution of nitric acid and distilled (chlorine-free) water, and diluted by three volumes of distilled water. The residue, which is gold, is filtered off and washed with dilute sulphuric acid and distilled water (1 part sulphuric acid to 15 parts water). The dilute nitric acid solution from the digestion and filtering contains silver ions, some mercury ions, and other ions in trace percentages. Hydrochloric acid or sodium chloride (table salt) is added to this solution to precipitate the ions—most of the precipitate produced will be silver chloride, with some mercuric chloride and traces of other chlorides. The chlorides are filtered off and washed with plenty of hot water to remove the majority of the mercuric chloride ($HgCl_2$) and lead chloride ($PbCl_2$). The silver chloride is then processed by one of the three methods described in the preceding section (see Figure 9.4).

Now you are ready to purify the gold residue. There are several directions or routes that you can take, two of which I will describe at length.

Route 1. Melt the gold into a cathode with borax and saltpeter flux. Test it to see if it is pure enough as is; if so, refine it in an electrolytic gold cell and cast the refined gold (the cathode) into a gold ingot. If it is not pure enough for the gold cell (when checked with our gold needles), but almost is, it can be brought higher in purity by dilution with pure gold. Then it can be cast into an anode, refined into a gold cell, and recast into a pure gold ingot.

Route 2. Digest the gold residue in aqua regia (one part nitric acid to three parts hydrochloric acid). Evaporate this to a syrup-like consistency, add hydrochloric acid, and reevaporate to the same consistency. Repeat this evaporation process three or more times; then dilute the solution and precipitate the gold ions from the solution with sulphur dioxide gas, copperas, or oxalic acid (your choice). Wash the precipitated gold, cast it into an anode, and purify it in a gold cell; or, redissolve the gold precipitate in aqua regia, take it through the multiple evaporations, reprecipitate the gold, and cast it into a pure ingot.

As you can see from the route taken with the mercury, gold, and silver amalgam, it is simpler to separate an amalgam of silver and mercury alone or gold and mercury alone than to separate an amalgam of all three elements.

Burden: Granulated Gold and Silver Alloy (Silver Less than 10%)

This gold–silver proposition applies to alloys that are not over 10% silver, with the remainder being gold. If the alloy is 15% silver, for example, add pure gold to adjust the percentage of silver downward. See Figure 9.6.

Step A: Digest the alloy in aqua regia (one volume of nitric acid to three volumes of hydrochloric acid).

Step B: Evaporate the solution to syrup, a minimum of three times.

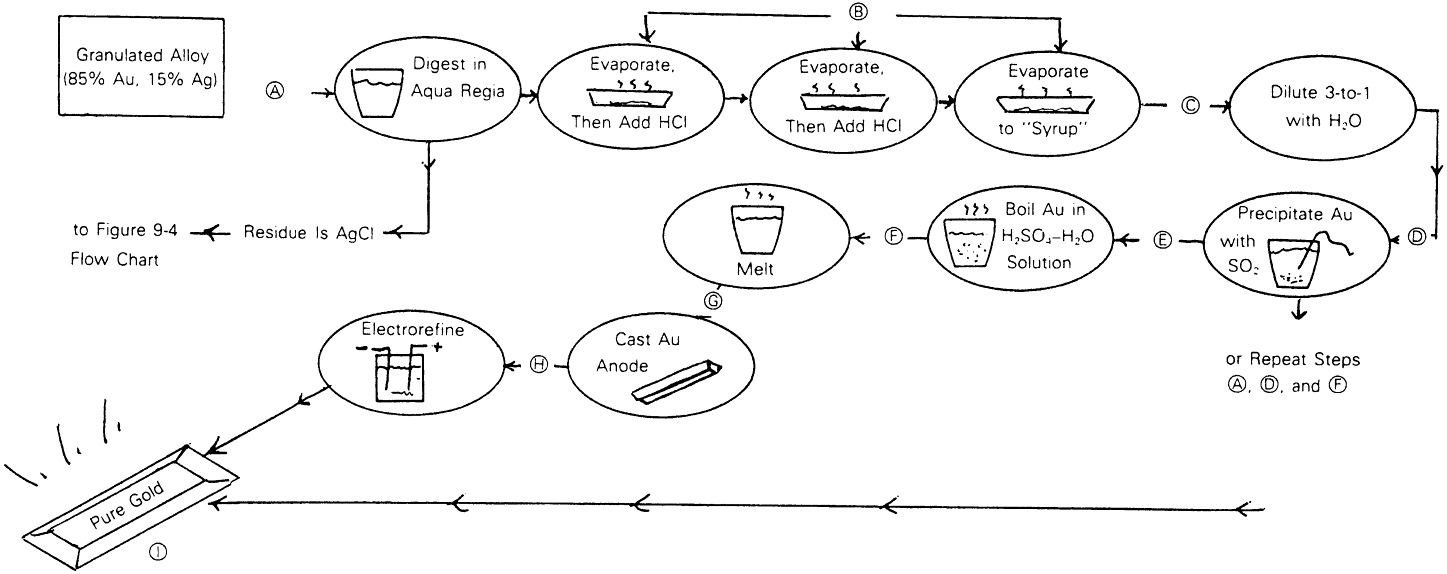


Figure 9.6. Flowchart for 85% gold, 15% silver alloy

Step C: Dilute the syrup with three to four volumes of water. Let the silver chloride settle, decant off the solution, wash the silver chloride onto a filter, and wash it with hot water; add this wash water to the decanted solution (gold chloride solution). Then, refine the silver chloride as shown in Figure 9.4.

Step D: Bubble sulphur dioxide through the solution to precipitate the gold. Filter the gold powder off onto a filter, and wash and then boil the gold powder in a dilute solution of one part sulphuric acid and one part water in a casserole dish. Wash the gold powder free of acid.

Step E: Decide which of the following options to take: to go on to Steps F, G, H, and I; or to take the precipitate back through Steps A, D, and F, and then (skipping Steps G and H) to move ahead to Step I. The latter option is a form of repurifying.

Step F: Melt the gold powder precipitate with an oxidizing flux of saltpeter and borax.

Step G: Cast the melted gold into an impure anode.

Step H: Refine the anode in a gold cell onto a pure gold starter sheet (cathode).

Step I: Melt the cathode and cast into an ingot of pure gold.

Burden: Gold–Silver Alloy (Silver 80% and Gold 20%)

See Figure 9.7. In this proposition, you have the option of refining the silver into a pure silver ingot (Steps A through F) or of producing silver chloride (Steps G and H) and then following the silver chloride refining procedure shown in Figure 9.4. In both cases, you wind up with the gold content in the form of a gold residue, which you process as shown in Figure 9.6.

Step A: Dissolve the granulated gold–silver in a solution composed of one volume of nitric acid and one volume of distilled water.

Step B: Dilute the solution by three volumes and filter off the residue, which is your gold content. This residue is treated according to the process shown in Figure 9.6.

Step C: Adjust the solution with nitric acid so that the silver ions are reduced to metallic silver, plating a pure silver starter sheet (acting as the cathode) in a conventional cell using a stainless steel anode.

Step D: Use this silver cathode as the anode in a Thum cell.

Step E: Refine the silver anode, wash the pure silver crystals, melt them, and cast the molten silver into a pure silver ingot.

You could, at Step B, precipitate the silver as silver chloride, dissolve the chloride in ammonium hydroxide, filter and reprecipitate it as silver chloride by using nitric acid as the precipitant, and treat it as purified silver chloride in the manner shown in Figure 9.4.

Steps F and G: Dissolve the granulated gold–silver alloy in hot sulphuric acid (H_2SO_4) solution—one part sulphuric acid to one part water, diluted by three volumes of water and filtered. The gold residue is then handled according to the steps in Figure 9.6.

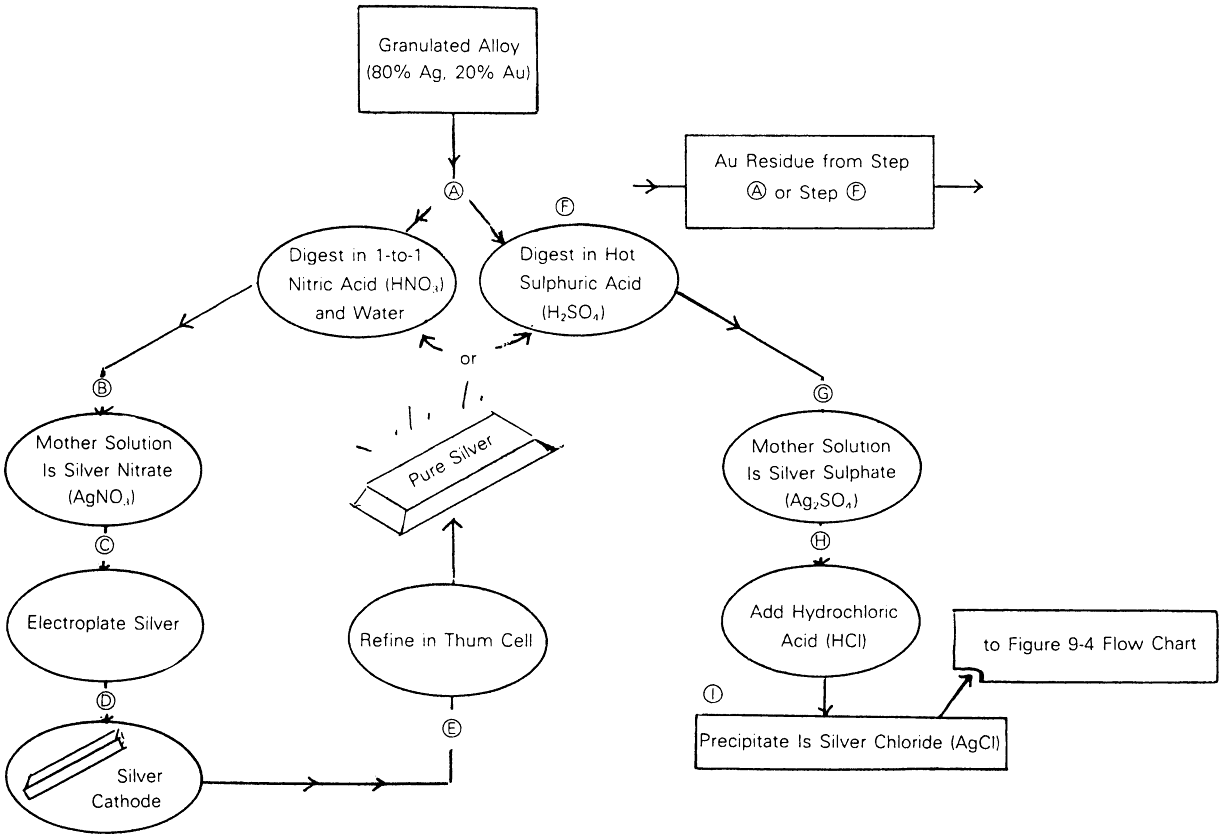


Figure 9.7. Flowchart for 20% gold, 80% silver alloy

Steps H and I: Add hydrochloric acid or sodium chloride to the solution and precipitate the silver as silver chloride. Filter, wash, and process this as outlined in Figure 9.4.

Burden: Granulated Gold, Platinum, and Palladium

See Figure 9–8.

Step A: Digest the granulated gold, platinum, and palladium in aqua regia (one part by volume nitric acid and three parts hydrochloric acid). Boil the solution until it is the thickness of syrup. Then, add hydrochloric acid and repeat the process a minimum of three times. It is important to expel all the nitric acid from the solution.

Step B: Dilute the solution by three or four volumes with water, allow it to settle, and decant most of it off, filtering the last to clear it of any sediments—such as insoluble silver chloride. Precipitate the gold with sulphur dioxide gas, copperas, or oxalic acid; run it off onto a filter, wash it well with hot water, boil it in 1-to-1 sulphuric acid and water, wash it again, and dry it. The gold can now be refined as shown in Steps F through I of Figure 9.6.

Step C: The solution, which now is free of gold, is treated by one of two methods to precipitate out the palladium. The first is to add to the almost boiling solution a few crystals at a time of sodium chlorate. The precipitate that is produced is palladium–ammonium chloride. The second method is to use DMG (dimethylglyoxime) [$CH_3C(NOH)CH_3$, butane dioxime].

The DMG method requires that, after the gold has been precipitated and removed, the solution containing the platinum and palladium be reboiled to its syrup-like state. The syrupy liquid is diluted with three to four volumes of distilled water; then, a reagent consisting of equal weights of commercial-grade DMG, distilled water, and alcohol is added to the warm solution until the palladium precipitate starts to drop. Then, an ounce or two of excess reagent is added. The precipitate is voluminous, yellow palladium glyoxime. This precipitate is gelatinous, so it should be filtered onto a filter and washed with a solution that is 60% alcohol, 10% hydrochloric acid, and the remainder water, and set aside to dry. See Figure 9.9 for the steps involved in processing the palladium further.

Step D: Boil the solution—now free of both gold and palladium—down, and add an equal volume of hydrochloric acid. If, for example, the filtrate containing the platinum ions is approximately 2 L in volume at the beginning of this step, then you will boil it down to approximately 1 L and add 1L of hydrochloric acid. Add to this hot solution a saturated solution of distilled water and sodium chlorate. Do this in approximately 25-ml (milliliter) portions. When all the chlorate solution has been added, boil the entire solution down to half its volume.

Step E: When it has cooled a bit, but is still quite hot (158°F or 70°C) add, for each quart (or liter) of solution you wish to treat, ½ lb. of ammonium chloride dissolved in hot water (use a good grade of ammonium chloride, and filter this

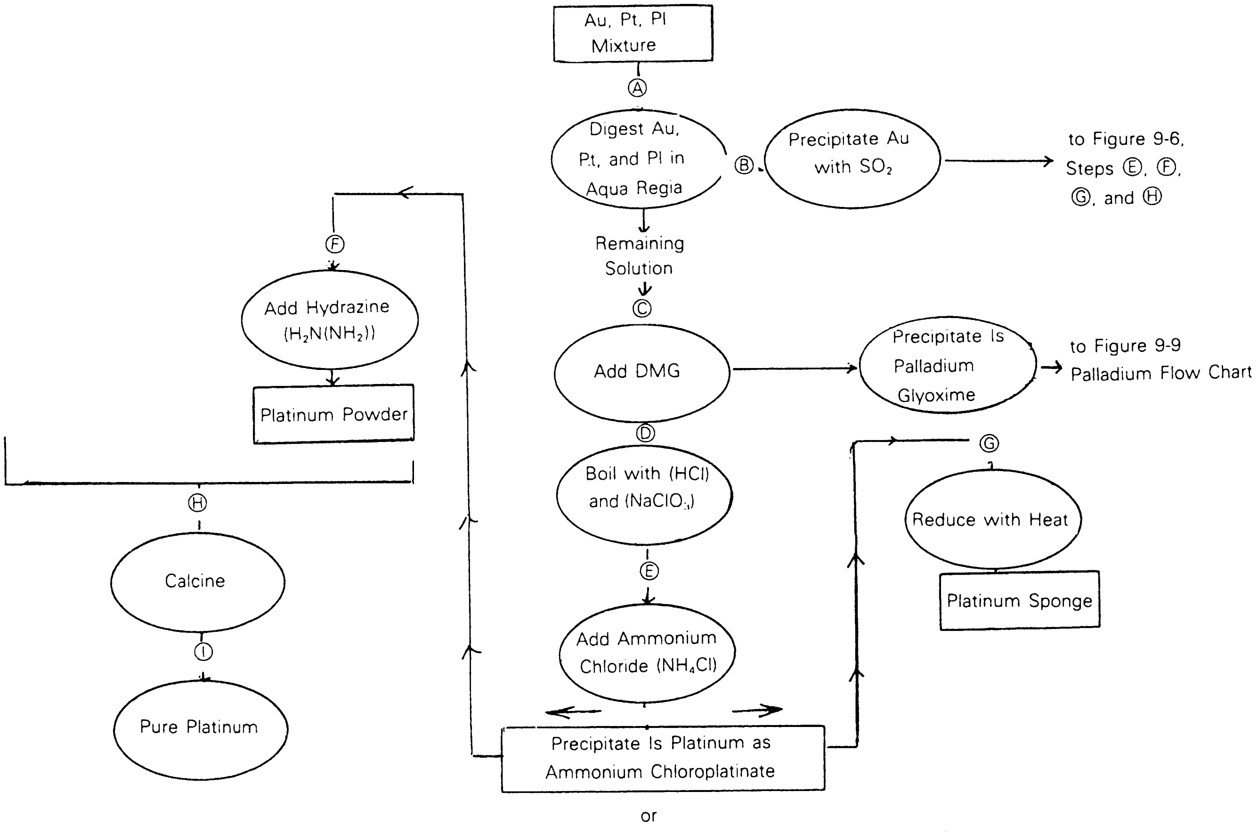


Figure 9.8. Flowchart for gold, platinum, and palladium mixture

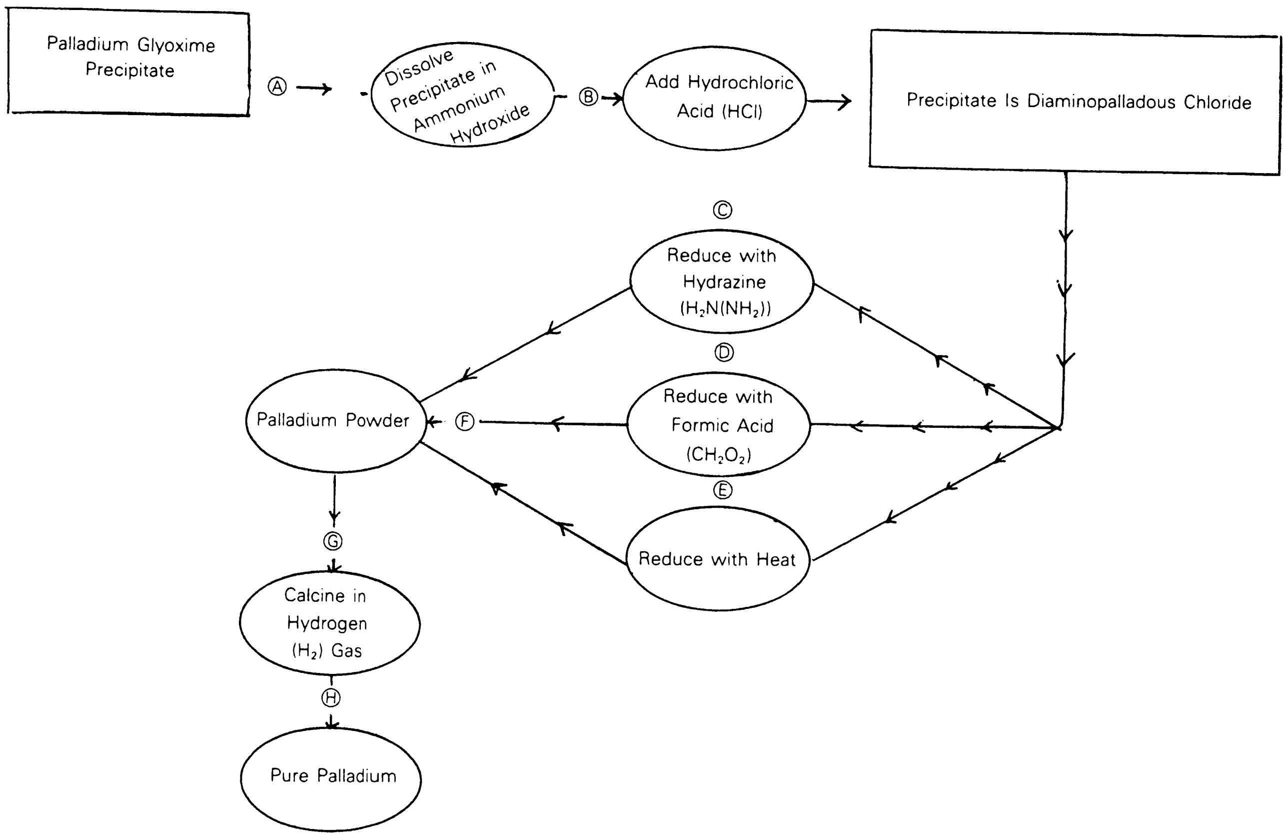


Figure 9.9. Flowchart for palladium glyoxime reduction

solution before using). This will precipitate the platinum as orange-red or yellow ammonium chloroplatinate. Ammonium chloroplatinate is also called ammonium hexachloroplatinate, platinic–ammonium chloride, platinic sal ammoniac, and platinum ammonium chloride. Its formula in chemical notation is $(NH_4)_2PtCl_6$. Use a spin bar during this operation. Filter the precipitate off onto a filter, and wash it well with a wash bottle filled with a saturated solution of ammonium chloride.

At this point, there are two directions you can take with the ammonium chloroplatinate: Step F or Steps G through I.

Step F: Mix the ammonium chloroplatinate precipitate with deionized water, in the proportion of 60–70 g of precipitate to 1 L of deionized water. Heat this solution to approximately 170°F (77°C). Keep the heated solution in a suspended slurry with a spin bar and add hydrazine $[H_2N(NH_2)]$ slowly until the ammonium chloroplatinate is reduced to metallic platinum—a heavy gray sand.

Hydrazine is a colorless, fuming, hygroscopic liquid that is explosive. Its flash point is only 126°F in an open cup. It is a strong reducing agent: The autoignition temperature is only 518°F, and combustion of hydrazine is highly exothermic. Hydrazine is highly toxic by ingestion, inhalation, or skin absorption and may explode if exposed either to heat or to a reaction with oxidizing materials. From this you can see that it is a dangerous, hazardous chemical that should be handled with utmost care.

Step G (as an alternative to working with hydrazine): Heat the ammonium chloroplatinate with a mild heat so that it releases white fumes under the hood. This drives off the chlorine, leaving behind the platinum.

Step H: The next move is called calcining or calcination. This, in reference to a metal, usually means strongly heating the metal in the presence of air to reduce the metal to a metallic oxide (roasting); in the present case, however, platinum is inert and will not oxidize. Dry the platinum that has been filtered from your solution and then place it in a fused silica evaporating dish and heat it to 1500°F (816°C) for 25 min.

Step I: The heating produces platinum sponge for use, for sale (if pure enough), or for repurification.

Burden: Palladium Glyoxime Precipitate

The following steps explain how to refine the product precipitated at Step C in Figure 9.8. See Figure 9.9.

Step A: Dissolve the palladium glyoxime precipitate in ammonium hydroxide, which produces a flesh-colored dichlorodiamine precipitate. With an excess of ammonium hydroxide, this precipitate will dissolve, leaving a clear solution.

Step B: Add hydrochloric acid to the clear solution, precipitating the palladium as a yellow diaminopalladous chloride called palladium yellow.

If you suspect the clear solution (palladium glyoxime dissolved in ammonium hydroxide) of carrying any gold or silver ions, you should add some sodium iodide to precipitate these as gold iodide (Au_3) or silver iodide (AgI). The usual procedure is to put about 2.5 cm (1 in.) of the solution in a test tube and check it for gold and silver with sodium iodide before treating the entire batch. This test should always be performed prior to adding the hydrochloric acid and precipitating the palladium yellow.

There are three ways to reduce the palladium yellow to metallic palladium: Steps C, D, and E of Figure 9.9 describe them.

Step C: Use hydrazine, as you did with the platinum yellow.

Step D: Reduce with formic acid [$HCO(OH)$], also called hydrogen carboxylic acid or methanoic acid.

Formic acid is a colorless, fuming liquid with a pungent, penetrating odor. Like hydrazine, it is a strong reducing agent. It is also a very hazardous chemical, with a flash point of 156°F in an open cup. Formic acid is extremely corrosive to skin and tissue; do not breathe its fumes, and above all *avoid skin contact*! Formic acid solutions are used in some flotation cells for ore concentration.

The formic acid reduction system works for both palladium and platinum. It offers the advantage that—when used with platinum or palladium precipitates (chloride salts)—there is little chance of metal loss, which can easily occur when the salts are reduced by being heated to drive off the chlorine. As I stated when covering direct reduction by heating, if your heat source gets the solution too hot and the fumes that appear are gray or black, you are losing values ("loss to fumes," it is called).

The other advantages of the formic acid system, besides zero metal loss, are no furnace is required, the method works quickly, it automatically removes most impurities, and the fumes produced are not very objectionable. It is also cheap. One slight disadvantage is that the reduction products (precious metals) are finely divided black powders, called platinum black and palladium black, which are not as easily handled as the familiar gray platinum and palladium sponges.

Use large, 2-L beakers, and only fill the beakers about one-quarter full of formic acid solution. If you are working with larger amounts, do not go to bigger beakers: Simply use several 2-L beakers.

For each ounce of platinum expected, weigh out 1 ounce of formic acid; for each ounce of palladium expected, weigh out 1½ ounces of formic acid. Pour the formic acid into a 2-L beaker, and slowly add enough water to dilute the acid by two or three volumes. Place a piece of litmus paper in the solution. (Note that in this exceptional case, water is being added to acid; *proceed with caution.*)

Add ammonium hydroxide (ammonia) slowly to the dilute formic acid solution, stirring constantly with a glass rod or spin bar. Work slowly. When the litmus just turns blue, stop adding ammonia. Now, add full-strength formic acid, drop by drop, until the litmus just turns red again. What you are looking for is a mixture of formic acid and ammonium hydroxide that is just slightly acidic. Fish out the litmus and discard it. In a separate 2-L beaker, place the palladium yellow (or platinum chloride) and cover it with about 1 in. of water.

Pour your formic acid–ammonia solution into a third 2-L beaker, until the beaker is about one-quarter full. You now have 2-L beakers that are about one-quarter full: one that you just put formic acid solution into, and one containing palladium yellow and water. Bring both beakers to a boil and slowly pour the boiling palladium yellow solution into the boiling formic acid–ammonia solution. The mixture is exothermic, so discontinue heating; the reaction will supply sufficient heat for completion.

When the palladium yellow solution touches the formic acid solution, it will foam up and turn black at once. The palladium black will settle quickly if it is pure; if it is contaminated (impure), however, it will settle slowly, and the solution will look like a mixture of black ink. If you still see yellow or brown, add some ammonia. If this does not reduce the yellow, add drops of the formic acid solution until all of the metal is precipitated.

If everything went as it should, the palladium black will now be on the bottom and the solution will be clear. If the solution is a faint, pale green, it could contain some copper or nickel ions in solution. This is not a problem. See Figure 9.10. The palladium black is filtered, washed with lots of hot water, and dried.

Step E: Reduce the palladium yellow by heating. The white fumes given off are departing chlorine; a free gray powder (palladium) will remain.

Step F: By one of the three preceding steps, you have reduced the palladium to a powder.

Step G: Calcine the palladium powder (or palladium black) as you did the platinum, with one exception: use a hydrogen atmosphere during calcining to prevent oxidation of the palladium at calcining temperature.

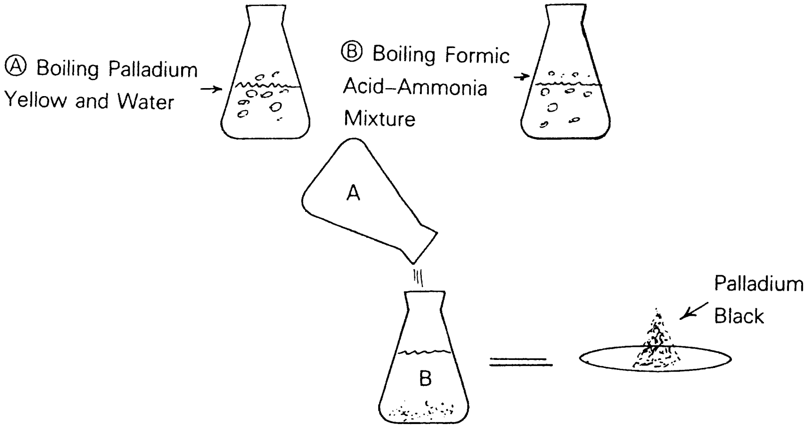


Figure 9.10. Reduction of diaminopalladous chloride precipitate with formic acid

Step H: The product, palladium sponge, is now ready for use, sale, or repurification.

Burden: Platinum–Iridium Alloy

I mentioned that iridium is precipitated along with platinum from an acid solution, but in a delayed action. If you want to eventually produce an alloy of platinum and iridium, which is a common alloy, you can let the platinum and iridium precipitates mix together. If you want the two metals separate, you can take advantage of a time delay between precipitations to separate the platinum and iridium. An alternative method of separating them is the zinc fusion method. See Figure 9.11.

Step A: Weigh the scrap platinum and iridium. Assemble three and a half times this weight in mossy zinc or zinc turnings.

Step B: In a graphite crucible, place the platinum–iridium scrap and the zinc in alternate layers. The bottom and top layers should be composed of ammonium chloride. Cover the crucible and seal it with wet asbestos. See Figure 9.12.

Place the crucible in the furnace and raise it to a white heat. Maintain this heat until there is no more evidence of ammonium chloride fumes. When the melt has cooled, remove the remaining button of platinum, iridium, and zinc.

Step C: Break up the button, which is quite brittle, into small pieces in a cast-iron mortar, or with a hammer, and wash the pieces with hot water.

Step D: Digest the granulated zinc, platinum, and iridium fusion in a 10% solution of hydrochloric acid. This puts the zinc into solution, leaving behind a residue of platinum and iridium. Filter this residue off and wash it free of acid. The zinc solution can be discarded or you can recover the zinc for use again.

Step E: Dissolve the platinum–iridium residue in aqua regia (one part nitric acid to three parts hydrochloric acid) and go through the usual steps of evaporation to syrup and addition of hydrochloric acid, and repeat three times.

Step F: Dilute the final, syrupy solution with two to three volumes of water, and then precipitate the platinum with ammonium chloride. The ammonium chloroplatinate precipitate is filtered off and washed with a saturated solution of ammonium chloride. It can then be handled as shown in Step F or Steps G through I of Figure 9.8.

Step G: Return to the remaining iridium solution.

Step H: Add hydrochloric acid to make the remaining solution (containing iridium ions) strongly acidic. Then boil the solution down to half its volume.

Step I: Add a little sodium chlorate to precipitate any palladium that is still present. Remove this by filtering.

Step J: Add a saturated solution of ammonium chloride to the filtered solution to precipitate the iridium as ammonium chloroiridate. Filter the precipitate off onto a filter, wash it first with a solution of ammonium chloride and then with water, and dry it.

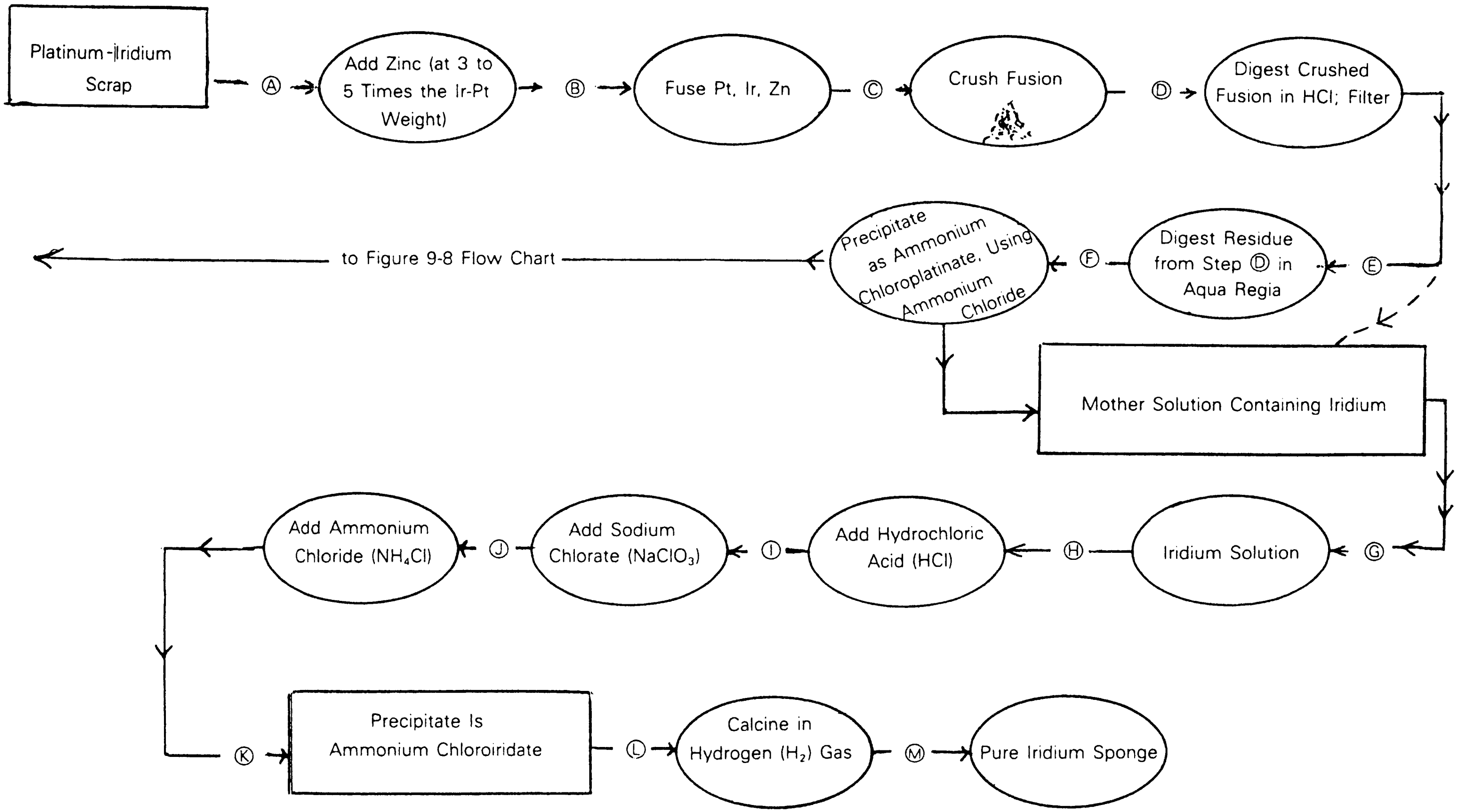


Figure 9.11. Flowchart for platinum–iridium scrap

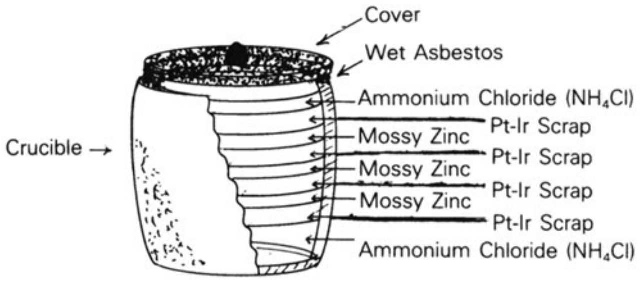


Figure 9.12. Crucible charge for platinum–iridium–zinc fusion

Step K: In Step J, the solution was boiling hot when you added the ammonium chloride. The solution should then be allowed to cool and settle for 10 or 11 h. The ammonium chloroiridate is then recovered, and the solution is reboiled, treated again with ammonium chloride, cooled, and settled for another 10–11 h, after which additional iridium precipitate is recovered. This procedure must be repeated until all the iridium is recovered; usually, three times is sufficient.

Step L: Reduce the ammonium chloroiridate to iridium sponge by driving off the chlorine with gentle heat or by calcining the salts in a fused silica dish in a hydrogen (H_2) atmosphere.

Step M: The product, iridium sponge, is ready for use or sale.

Burden: Ruthenium

Ruthenium is widely used as a hardener in platinum and palladium alloys. It has a Brinell hardness number of 220 as cast. This compares to Brinell hardness numbers of 60 for red brass and 724 for carbon steel. Ruthenium is recovered by distillation. The recovery system given here for ruthenium is the same whether the alloy is ruthenium and platinum, or ruthenium and palladium, or platinum, ruthenium, palladium, and iridium. See Figure 9.13.

Step A: Dissolve the material in heated aqua regia, keeping the mix down to a minimum of nitric acid and hydrochloric acid to do the job. Be very careful to avoid any boiling at this point, as boiling would result in a loss of ruthenium.

Step B: When everything is in solution and you have destroyed any nitrates with the hydrochloric acid, allow the solution to cool, and then raise the pH to a point at which it is just alkaline, using sodium or potassium hydroxide. If excessive hydroxide is added, metallic hydroxides will be precipitated. If this happens, add sufficient hydrochloric acid to redissolve the hydroxides, and start over with the hydroxide additions. Next, place the solution in a still. See Figure 9.14.

Step C: In Figure 9.14, I show two different arrangements for stills. One arrangement uses light air pressure to increase vaporization in the reaction chamber of the still. The other arrangement is a vacuum still, in which the vacuum pump

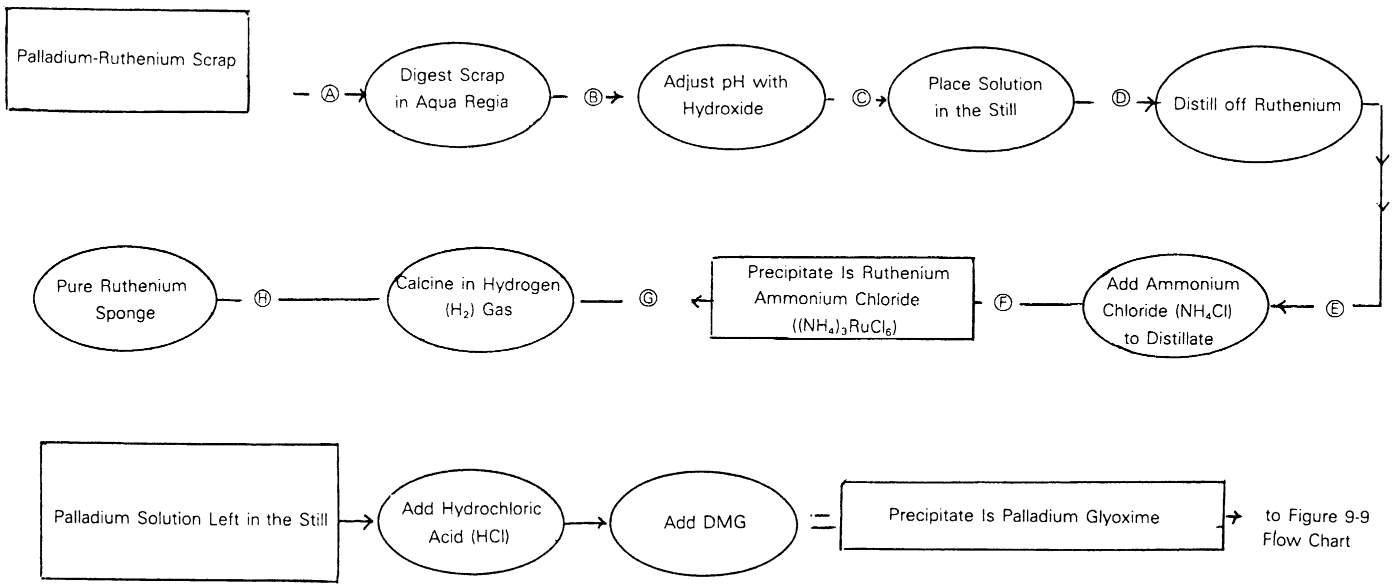


Figure 9.13. Flowchart for palladium–ruthenium scrap

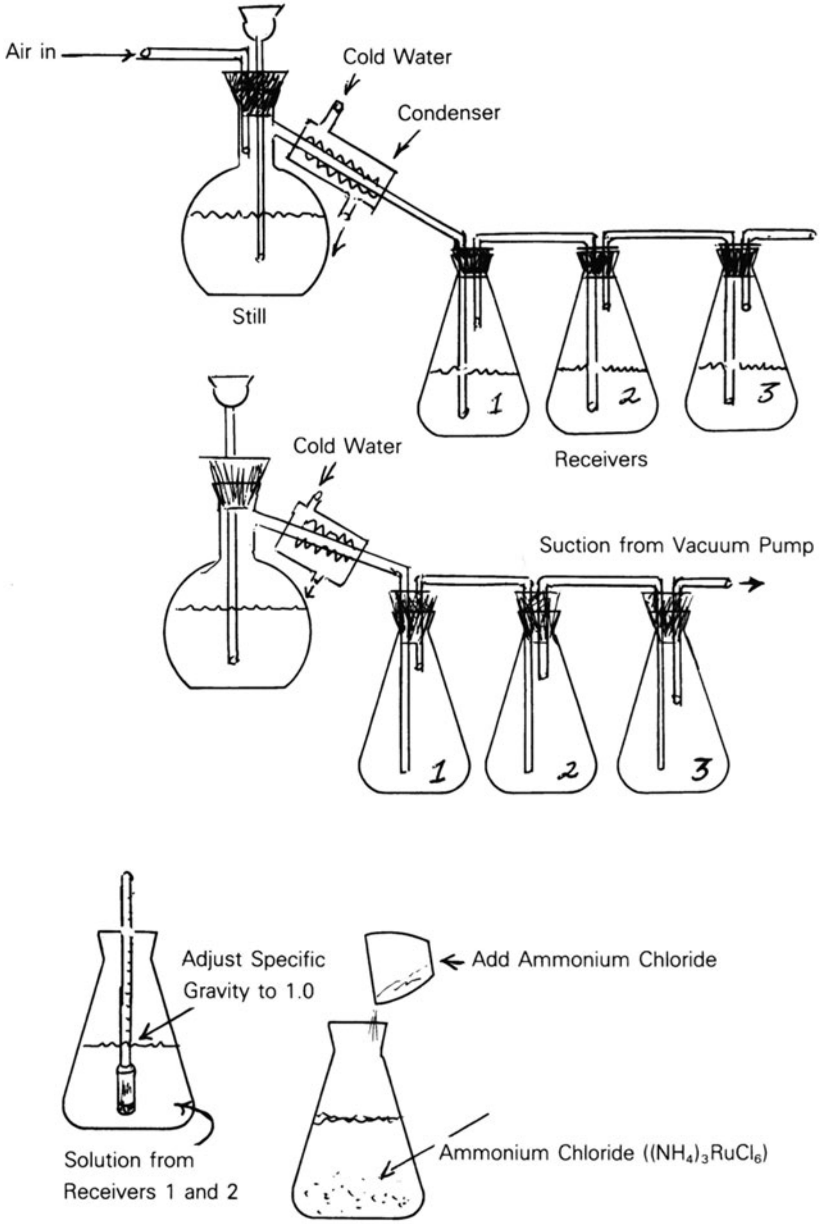


Figure 9.14. Ruthenium still arrangement; ruthenium precipitate

is protected from ruthenium trichloride vapors by the third receiver containing a caustic solution to neutralize the vapors. With either still, the operation is the same.

Step D: Fill receiver 1 and receiver 2 about two-thirds full of 4 *N* hydrochloric acid (HCl) solution. Fill the third receiver two-thirds full of a 50% sodium hydroxide solution to which 100 ml of ethyl alcohol have been added.

Heat the mother solution in the reaction vessel to 194°F (90°C). Add sodium hypochlorite reagent ($NaOCl \cdot 5H_2O$, drop by drop, to the solution in the reactor throughout the distillation process until no more ruthenium tetroxide is visible and the foam in the reaction vessel is nearly white. Sodium hypochlorite is very unstable in air and is usually mixed with sodium hydroxide and stored and used in solution. You can purchase it from your chemical supplier as a 5% reagent solution.

The end point of the distillation is indicated when a strip of filter paper that has been dipped in hydrochloric acid and thiourea solution retains no blue color when exposed to the vapors above the reactor solution. Thiourea is also called thiocarbamide [$(NH_2)_2CS$].

The hydrochloric acid and thiourea solution consists of a hydrochloric acid solution mixed with a 10% aqueous solution of thiourea to give the combined solution a 5% thiourea value. The liquids from receiver 1 and receiver 2 are combined and evaporated to approximately 1.0 specific gravity and heated to approximately 158°F (70°C). See Figure 9.14.

Step E: Precipitate the ruthenium with a saturated solution of ammonium chloride.

Step F: Run off the ruthenium precipitate onto a filter and wash it, first with ammonium chloride solution and then with water.

Step G: Calcine the ruthenium precipitate in a hydrogen atmosphere at 1500°F (816°C) to ruthenium sponge.

Step H: The ruthenium sponge is now ready for sale, use, or re-refining.

The solution from the reaction vessel and the solution that you just stripped of ruthenium can be put into the stock pot or treated. To treat the solutions from this and similar operations, combine the solutions and dilute with a 6 *N* hydrochloric acid solution. Then you can go after the values with ammonium chloride for platinum and iridium and with DMG (dimethylglyoxime) or sodium chlorate for palladium.

Stock Pot Procedure

I have suggested several times that you set up a stock pot to collect liquids and residues from various acidic extractions, spot tests, blow pipe fusions, and so on. I also advised you to save, in another pot, all your used filter papers from all filtrations and spot tests, paper towels used to wipe up spills, and other impregnated papers. A third stock pot should be filled with cyanide extractions and tests. With the cyanide residue solutions, it is not wise to accumulate too great a bulk; they should be treated each time you accumulate a liter or two.

Spent cyanide solutions from electrowinning cells, foul cyanide plating solutions, and cyanide stripping solutions are also relegated to the cyanide stock pot. Spent acid pickling solutions, spent or foul solutions from Thum cells, and other acidic residues are relegated to the acid stock pot.

The Acid Stock Pot Treatment

I think it is unwise to collect more than about 3 gal of liquid in an acid stock pot prior to treatment. The stock pot is a puzzle because you do not know how much of the value is in solution and what the acid content (concentration) is.

Your first step is to throw a handful of mossy zinc into the stock pot, stir it, and watch for bubbles. If no bubbles appear, add hydrochloric acid, an ounce at a time, stirring between acid additions. When you see some bubbling action, stop the acid additions. Be careful not to let this action build up too fast: The action is exothermic and can become hot enough to destroy the pot or boil over.

Let the solution work for a few hours; stir it often. Then check the top solution for values on the spot plate with stannous chloride. If the solution is still carrying values, or if it becomes thick and muddy, add more zinc and more hydrochloric acid. What you are looking for is a clear, pale green, almost colorless top solution, with the values on the bottom as a black powder. When the top liquid has reached this pale green color, you can safely assume that the values have all been precipitated. Dip or siphon off the clear to greenish liquid and discard it. Run the remaining liquid and black powder off onto a large vacuum filter. Wash the powder well with water and set it aside on the filter paper to dry. See Figure 9.15.

The Filter Stock Pot Treatment

You only need to save the contaminated areas of filter paper. Pinch them off and discard the uncontaminated portions. This usually applies to cone papers; the flat papers used in the Buchner funnel are saved intact. The papers are placed in a large cast-iron frying pan, doused lightly with gasoline, and burned. After

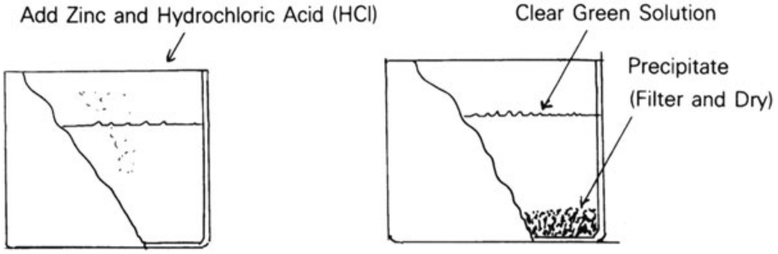


Figure 9.15. Zinc ion exchange with values in stock pot

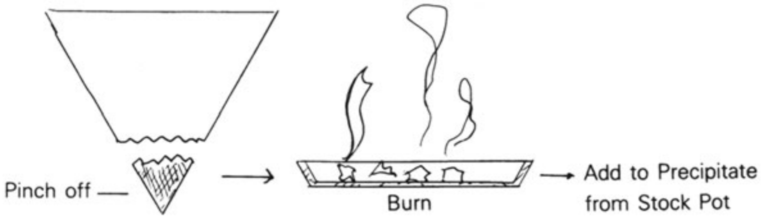


Figure 9.16. Handling used filter papers

the first burning, more gasoline is added and the material is burned again. The residue from the burning is collected and added to the black powder that was precipitated by adding zinc to the acid stock pot. See Figure 9.16.

The Cyanide Stock Pot Treatment

The cyanide solutions are collected in a relatively small (1 or 2 L) quantity in another stock pot. Adjust the pH to about 12 or 13 by adding potassium hydroxide to the combined solution. Add powdered or mossy zinc and stir to precipitate any gold or silver ions as metallic slime. When doing this, hang a slab of zinc in the solution to prevent the gold and silver from redissolving. You will also precipitate various base metals that were present as ions in the solution. This process requires about 2 ounces of zinc per ounce of gold in solution.

This solution, like the acid solution, should clear as the metallic values drop out, until the top solution is a clear, light green. Filter and wash the residue free of any cyanide with lots of water and add it to your black powder from the acid stock pot and your filter incineration residue. See Figure 9.17.

An alternative method is to filter the solution, adjust the pH, and plate out the metallic ions in a steel wool cell, afterward washing the steel wool free of cyanide. Next, digest the steel wool with sulphuric acid solution (1 volume of sulphuric

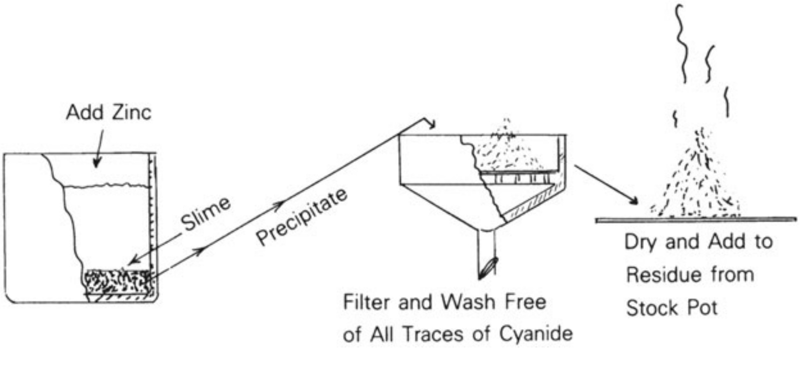


Figure 9.17. Zincing cyanide solutions

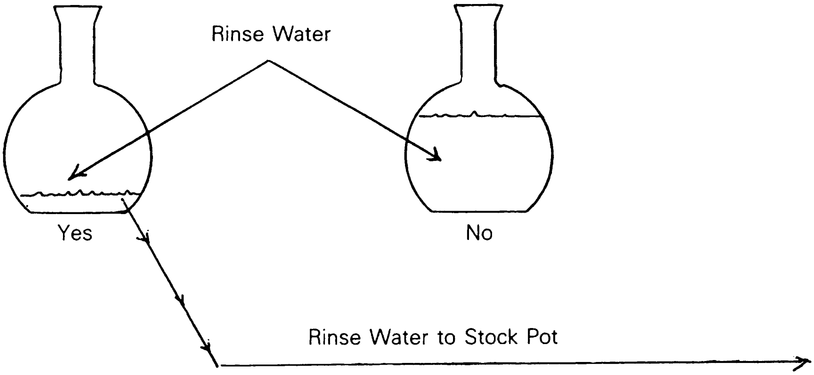


Figure 9.18. Rinsing glassware

acid to 15–20 volumes of water); then melt and granulate the residue, process or cast it into an impure anode, and refine it in a cell. If this is your choice, add enough copper to make it a copper proposition in a cell.

The slimes, muds, powders, and sludges you recover from your two stock pots and your used filters can be very valuable. Never neutralize and discard any solutions without spot testing them for value. Whenever you finish using a test tube beaker, flask, still, or spot plate, hold it over the appropriate stock pot and, with a wash bottle, rinse it into the stock pot. Crucibles, scorification dishes, assay cupels, and slags from fusions and meltings are all ground up; the light material is then panned off with a gold pan and the residue goes into the appropriate stock pot.

A small amount of rinse water swished around in a flask or beaker will do a vastly better job of picking up values than a large amount of water that is simply poured in and poured out. Two light rinses will do the trick. See Figure 9.18.

Step-by-Step Procedure for Multiple-Value Burden

I have covered various combinations and some alternate routes you can take in refining gold, silver, platinum, palladium, iridium, ruthenium, rhodium, and osmium. Now I will describe a procedure for a batch that contains all eight of these values. The material could be in the form of black powders and sludges from stock pots, slimes from refining cells, or a granulated alloy mixture.

See Figure 9.19. The wet chemical extraction method given here is accepted as the usual method of handling these multiple values. However, there are other ways to extract them, and there are various types and arrangements of physical equipment to accomplish these extractions.

Step 1: Digest the material in aqua regia (one part nitric acid to three parts hydrochloric acid) and boil the solution down to a syrup-like consistency. This

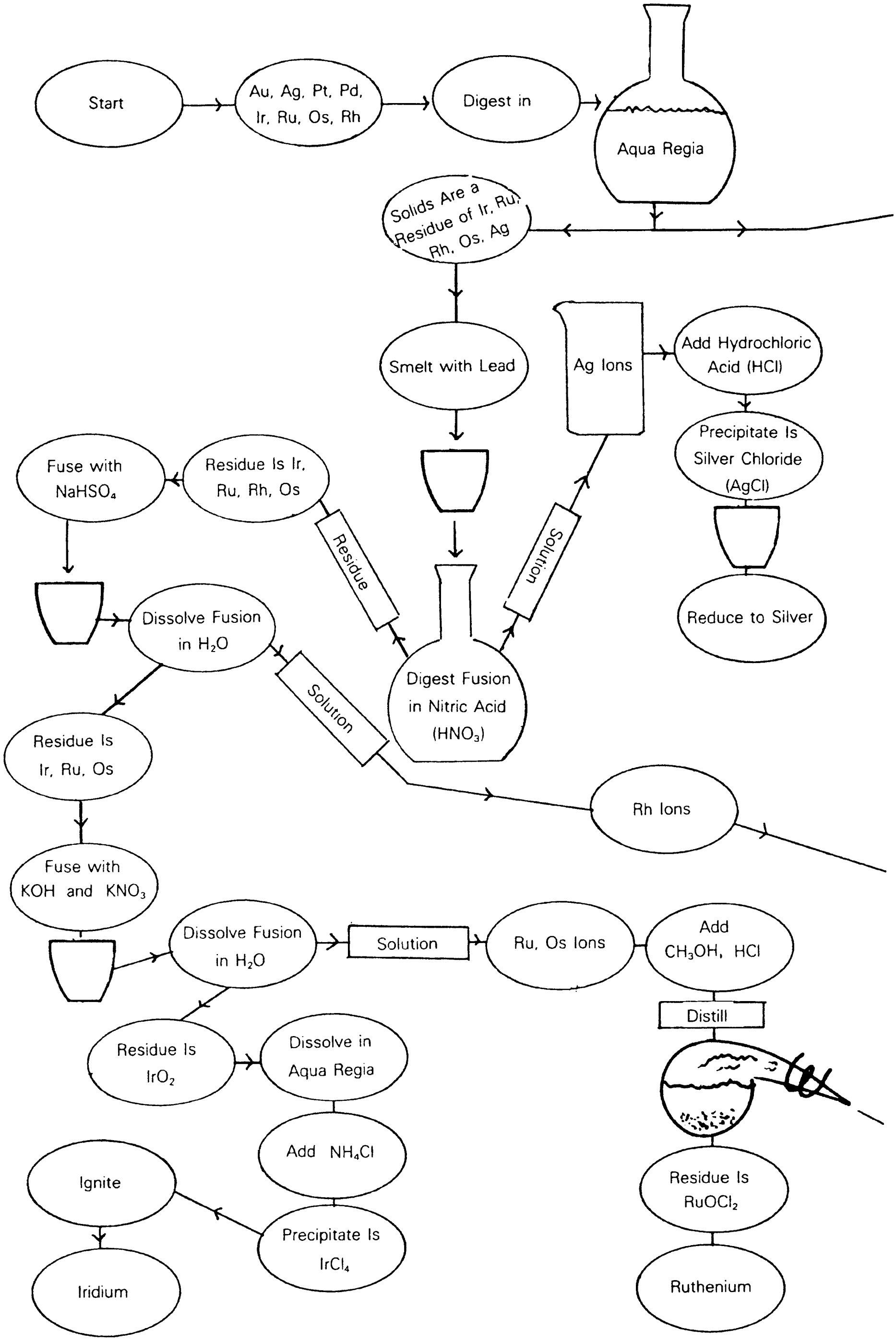


Figure 9.19. Master plan for wet chemical extraction

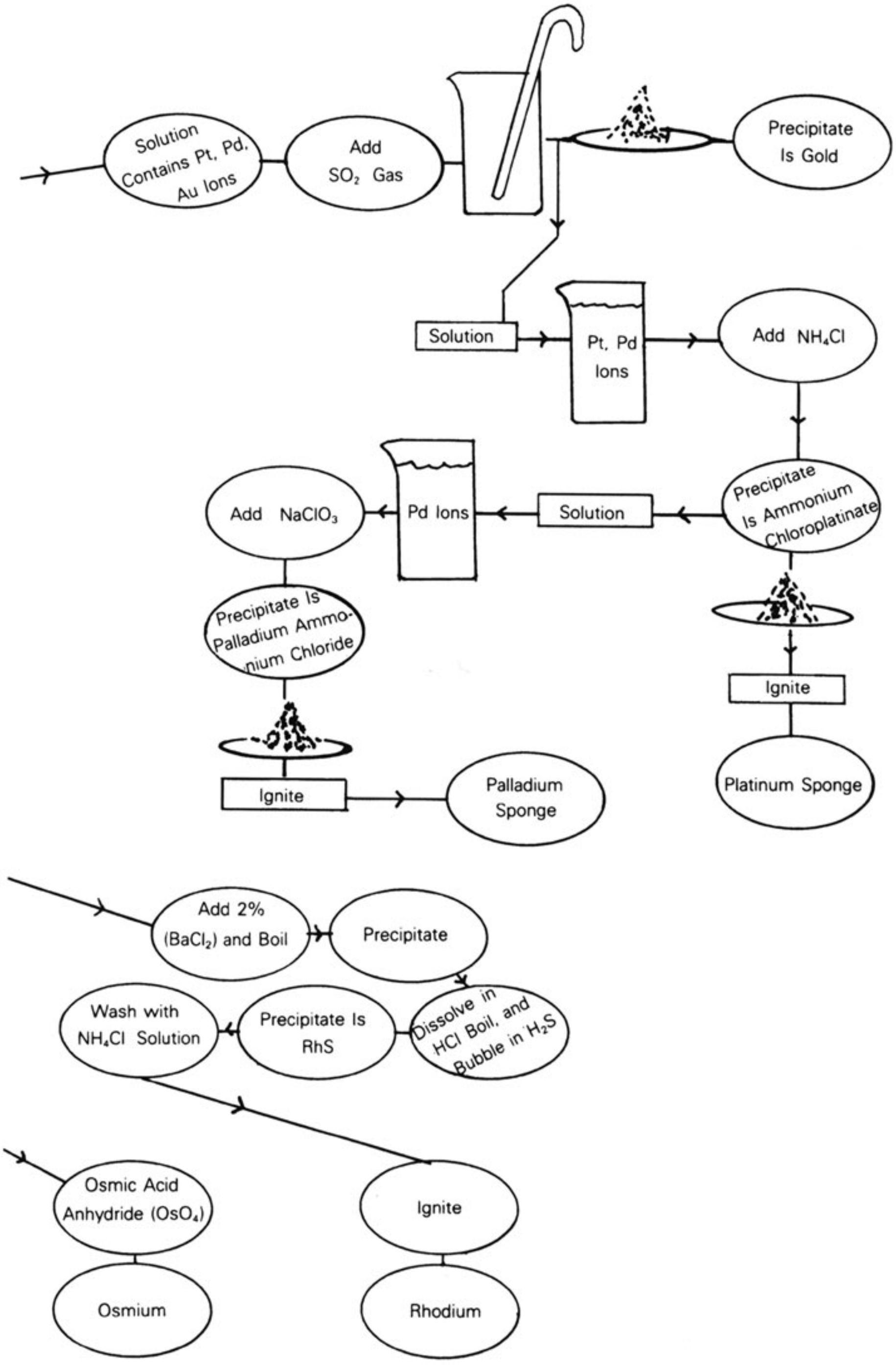


Figure 9.19. Continued

evaporation is repeated three times, with the addition of hydrochloric acid after each evaporation.

Step 2: Dilute the last evaporation with three or four volumes of water and filter it. The residue on the filter is iridium, ruthenium, rhodium, osmium, and silver chloride. The original solution contains platinum, palladium, and gold in solution.

Step 3: Bubble sulphur dioxide gas through the platinum, palladium, and gold solution. This precipitates the gold as a brown powder. Filter the solution; wash, dry, and set aside the precipitated gold for purification.

All washings should be added to the pregnant original solution at each precipitation.

Step 4: The solution, stripped of gold values, contains platinum and palladium. Add a saturated solution of ammonium chloride to the mother solution to bring down the platinum as ammonium chloroplatinate, an orange powder precipitate. Filter this from the solution, wash it, and set it aside for reduction to platinum sponge.

Step 5: The solution should now contain only palladium values. Add sodium chlorate crystals to the solution to precipitate the palladium as palladium ammonium chloride, a red powder precipitate. Wash, dry, and set this aside for reduction to palladium sponge.

The solution should be valueless: spot test and discard it. It will show traces of platinum regardless of how complete your precipitation was.

Step 6: Fuse the residue of iridium, ruthenium, rhodium, osmium, and silver chloride from the aqua regia digestion with lead.

Step 7: Granulate and digest the lead fusion in nitric acid; then dilute the solution and filter it. The residue on the filter is iridium, ruthenium, rhodium, and osmium. Strip the solution of its silver ions by adding hydrochloric acid or table salt, which precipitates the silver as silver chloride ($AgCl$). Filter the silver chloride from the solution, wash it, and dry it. It is stored in the dark until ready for reduction to metallic silver by cementation or by flame reduction followed by purification in a Thum cell. The solution is spot tested and discarded.

Step 8: Fuse the residue from Step 7 with sodium bisulphate. Grind up the fusion in a cast-iron mortar and dissolve it in water. The rhodium is now in the water extraction, and the iridium, ruthenium, and osmium form a residue in the water extraction. Filter off the residue, wash it on the filter, and set it aside. Place the solution and the wash water containing the rhodium in a clean flask.

Step 9: To the water extraction, add 2% barium chloride ($BaCl_2$) solution and heat. This should cause a precipitation. Bring the solution and precipitate to a boil, and boil them for several minutes.

Step 10: Allow the solution and the precipitate to cool, run the precipitate off onto a filter, and wash it, first with a solution of hot water and barium chloride and then with distilled water.

Step 11: Transfer the precipitate (designated as the #1 precipitate) to a clean flask and add a solution of one volume of hydrochloric acid and three volumes of distilled water to it. Heat this until the precipitate is in solution.

Step 12: When the precipitate is in solution, raise the temperature to boiling and bubble hydrogen sulphide through the solution slowly. This will precipitate the rhodium as rhodium sulphide. The precipitation should take 35–50 min to complete.

Step 13: Filter off the rhodium sulphide at once onto a filter and wash it with dilute ammonium chloride.

Step 14: Dry and reduce the rhodium sulphide to metallic rhodium, using low ignition; cool it under a stream of hydrogen.

Step 15: Fuse the residue of iridium, ruthenium, and osmium from Step 8 with a flux composed of 50% potassium nitrate (saltpeter) and 50% potassium hydroxide. Crush the fusion and extract the water-soluble elements with water.

Step 16: This extraction leaves the ruthenium and osmium in the aqueous solution and the iridium as iridium oxide. Filter off the iridium oxide and wash it with water.

Step 17: Dissolve the iridium oxide in aqua regia and then add ammonium chloride to form iridium chloride ($IrCl_4$). Filter this precipitate, wash it with dilute ammonium chloride and then with water, and dry it.

Step 18: Reduce the iridium chloride to metallic iridium by ignition under the hydrogen torch or in a hydrogen atmosphere. All your ignitions or reductions of metallic salts—such as platinum chloride and rhodium sulphide—are easily made with a standard hydrogen melting torch. The ignition is done in a crucible in exactly the same manner that you did the ignition for platinum chloride, except that, when the chlorine (the white fumes) is driven off completely, the metallics are allowed to cool under the cool hydrogen gas from the unlit hydrogen torch.

When the chlorine has been driven off (no more white fumes), raise the temperature in 150°F increments (at intervals of 5 min) from a starting temperature of 700°F until the iridium reaches a red heat. Cut off the heat source and light the hydrogen torch—just the hydrogen: Leave the oxygen off. Play this hydrogen flame, which is reddish yellow, across the cooling iridium until the metal loses its visible red color. Extinguish the hydrogen flame by turning off the hydrogen valve. Turn the hydrogen valve back on but without igniting it. Play the unlit cool hydrogen over the iridium until it has cooled to room temperature. See Figure 9.20.

Great care must be exercised when you perform the final cooling with unignited hydrogen. The entire operation must be done under the hood with all fans and switches off. There must be nothing in your entire work area that could possibly cause a spark or that could in any way cause the hydrogen to ignite. Hydrogen is extremely explosive with the proper mix with oxygen.

Step 19: Place the solution containing the ruthenium and osmium ions in the reaction vessel of the still. Distill the osmium across to the receiver as osmic acid anhydride (OsO_4), which can be reduced to osmium in a hydrogen atmosphere. The reaction is heated to redness; the residue left in the reaction side is the ruthenium. See Figure 9.21.

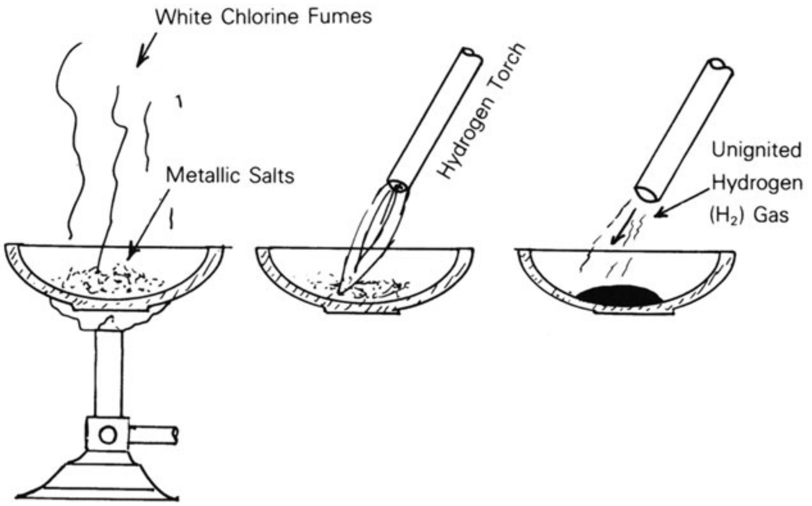


Figure 9.20. Sponge reduction under hydrogen gas

The chemical reagents necessary to do the complete 19-step procedure given above are aqua regia (one volume of nitric acid and three volumes of hydrochloric acid), litharge (PbO) or lead for fusion, ammonium chloride (NH_4Cl), sodium chlorate ($NaClO_3$), sodium bisulphate ($NaHSO_4$), potassium nitrate (KNO_3), potassium hydroxide (KOH), methyl alcohol (CH_3OH), barium chloride ($BaCl_2$), hydrogen gas (H_2), and sulphur dioxide gas (SO_2).

In most cases, if you are buying dental or jewelry scrap, you will identify and separate the material into groups as pure metals and into subgroups as various alloys, which you would treat separately. In this way, you can avoid having to go through all of the tedious 19 steps set out above.

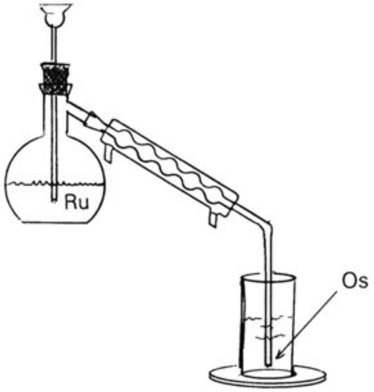


Figure 9.21. Still setup for osmium

Warning: In any operation involving osmium, especially one involving direct or indirect heating of osmium or a compound of osmium, work under a hood with sufficient draft. You must protect your face, eyes, and throat against osmium. The very pungent garlic odor produced by osmium is osmium tetroxide (OsO_4). The word osmium is from the Greek word for stench. The fumes produced by heating osmium, or the natural alloy of iridium and osmium (called iridosmine), if allowed to come in contact with eye tissue, reduces to metallic osmium as a deposit on the eye tissue. This can produce *blindness*.

With most residues, particularly low-value ones, concentration is the key to a viable operation. With muds and slimes from a stock pot or slimes from electrorefining cells or testing, the most general procedure is to dry the slimes and mix them with charcoal, flux, and litharge, then to make a lead fusion (the lead collecting the values), and then a cupellation to convert part of the lead back to litharge for reuse.

The lead fusion should not be cupelled to litharge completely (that is, until litharge ceases to form). If the lead is cupeled completely, you can wind up with a hardened metal material that is not readily attacked in the subsequent operation. Your aim should be to remove excess lead, leaving behind a lead alloy rich in precious metal values.

Cupel off only about one-third of the lead, and granulate the remaining lead. Boil the granulation in concentrated sulphuric acid to remove most of the silver and about one-third of the palladium as sulphates. This leaves a residue containing gold, platinum, ruthenium, osmium, and perhaps other precious metals, easily accessible to the aqua regia. Then you simply follow the flowchart shown in Figure 9.19.

The gold, platinum, and palladium are removed in the usual manner, using sulphur dioxide for the gold, ammonium chloride for the platinum, and sodium chlorate for the palladium. The ruthenium is separated with sodium bisulphate.

Fuse the residue (iridium, ruthenium, and osmium) with caustic potash (KOH) and potassium nitrate (KNO_3). This should be done in spun iron bowls at a dull red heat, converting the ruthenium into soluble potassium ruthenate. Dissolve the fusion in water and treat it with hydrochloric acid. This converts the potassium ruthenate into volatile ruthenium tetroxide, which is easily distilled and collected in dilute hydrochloric acid containing methyl alcohol.

When the contents of the receiver from the still are evaporated, the product is ruthenium oxychloride ($RuOCl_2$), which is easily reduced to metal by ignition in a hydrogen gas atmosphere. The osmium tetroxide (OsO_4) is also reduced under hydrogen.

With most solutions containing metallic ions of value, precipitating the ions in the form of a mud, using zinc ion exchange, is usually the least expensive and best way to go.

10

Various Systems

In this chapter, I will present a very low-tech explanation of the various refining systems that are available. It is the little things that are left out of instruction manuals that often cause the most serious problems.

The Cyanide Process

The cyanide process has been around since 1889. The first commercial operation using it was at the Crown Mine in New Zealand. It is widely used today, in many different physical arrangements. It is extensively used as a collecting medium for gold and silver, and in some cases, it is used to extract copper from copper ores that also carry some gold and silver. The descriptions that follow apply to the typical method of application.

Some ores require roasting prior to treatment with cyanide. Some require extremely fine grinding in order to release their values so that the cyanide can make contact. Other ores need only be crushed to a size as large as walnuts to give up their values to cyanide.

The time element required for complete extraction can vary from a few hours to a week or more, depending on a variety of factors.

One problem with using finely ground ore is the channeling of the solution through the ore. See Figure 10.1. Ores that carry excessive cyanide-destroying elements—such as copper, arsenic, antimony, and manganese, in some of their forms—may be impossible to treat with cyanide.

The ideal ore would be one that is completely oxidized without containing any cyanide robbers and that gives up its values quickly following a simple treatment of a rather coarse crush.

Most ores have to be treated with lime to destroy (neutralize) any acid salts. Any acids present will react with the cyanide when it is added to form deadly

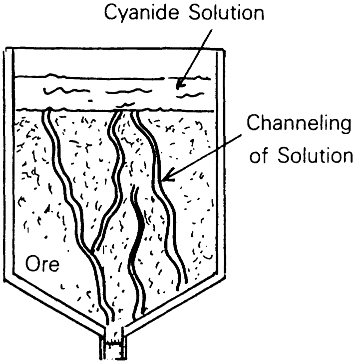


Figure 10.1. Channeling of leach solution

hydrocyanic gas. Aside from the danger involved, this reduces the amount of cyanide available to combine with the values.

The amount of lime necessary is determined by the acidity of the ore to be treated. This can be established by taking a weighed sample of the ore, mixing it with water, and adding lime a little at a time—keeping track of the additions (weight)—until the pH is about 12. From this, it is easy to approximate the amount of lime per ton of a given ore that you will need.

The simplest method of cyanide extraction uses a tank called a brown or Pachuca tank. See Figure 10.2. The ore is crushed to the desired size, the required lime and water are added, and the now basic ore is placed in the Pachuca tank.

The cyanide solution consists of a few pounds of potassium cyanide per ton of water: approximately 250 gal of water and 5 lbs. of potassium cyanide. In most cases, the cyanide solution is added to the ore and allowed to soak for several hours before the leaching is commenced. The leaching consists of adding

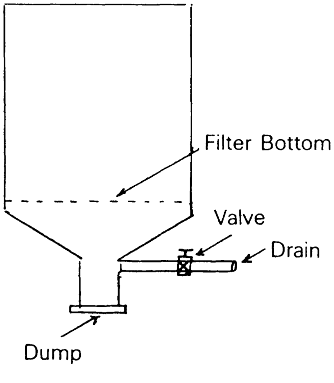


Figure 10.2. Pachuca leach tank

fresh cyanide solution to the top of the material, while drawing the pregnant solution off at the bottom.

The drawn-off solution is stripped of its values by being run through zinc shavings that are held in boxes called precipitation boxes. The ion exchange takes place in these boxes: The zinc goes into solution in place of the gold and silver, which are recovered as slimes and processed (usually) into doré bars for electrorefining. The design of the zinc precipitation boxes, like that of the other equipment, can take many different forms. The basic precipitation box is quite simple. See Figure 10.3.

The key is to construct the boxes in such a way that the gold- and silver-bearing solution must come into immediate contact with large numbers of the zinc shavings. The leaching is continued until the solution being drawn off at the bottom does not assay in gold and silver.

The gold and silver values can be recovered by running the solution through a column of activated charcoal, which will strip the solution of these values. The charcoal can be relieved of the values by burning or by extraction with hot sodium hydroxide solution. The carbon (charcoal), after being stripped with hot (90°C) sodium hydroxide, is reactivated in a rotary kiln for reuse.

Heap leaching is simply the leaching of a pile of crushed ore that has been placed on a sloping pad which has been made impermeable with sheet plastic, asphalt, or clay. The leach pad is sloped so that it can be drained at the toe. See Figure 10.4. The ore is crushed to approximately 2 in. in diameter and piled to a height of from 10 to 30 ft. The top is made level. The ore is sprayed with the cyanide solution, and the pregnant solution is drawn off at the toe.

The carbon-in-pulp process was invented by F. McQuiston and T. Chapmann in 1946. It uses coarse charcoal confined in rotating baskets or screened containers that allow the agitated cyanide pulp of slimy ores to come into contact with the carbon. The rotating carbon containers strip the solution of its values. This is an extremely simplified representation of the process: It is actually quite involved. It has been used by Golden Cycle of Cripple Creek, Colorado, and at Homestake in South Dakota. The Soviet Union has a similar system that uses ion-exchange resin in place of activated charcoal; it might properly be called a resin-in-pulp system.

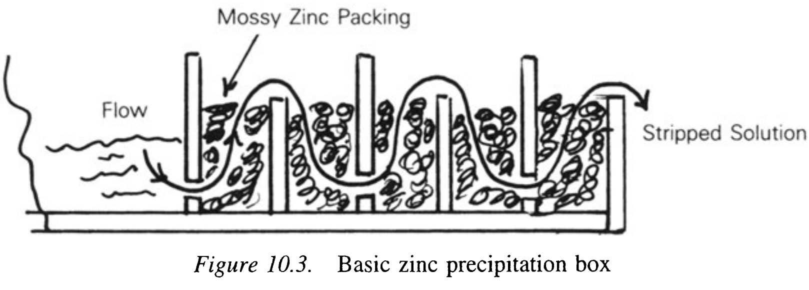


Figure 10.3. Basic zinc precipitation box

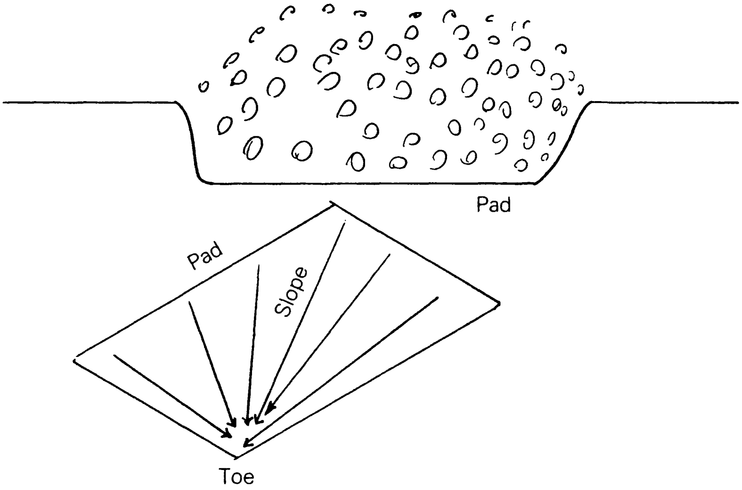


Figure 10.4. Basic leach pad

In the carbon-in-pulp system, the charcoal is stripped of values with hot cyanide solution under pressure. The resulting solution is stripped of values on steel wool in a series of electrostripping cells. Each cell contains 12 lbs. of steel wool as a cathode, each of which will hold up to 1200 ounces of gold. The plating voltage is 4 V DC at 40 A of current.

The most successful ores for extracting by cyanide leaching are those that are free-milling.

Silver is less soluble in potassium cyanide solutions than gold. When an ore contains appreciable amounts of silver, the addition of table salt (sodium chloride) will help alleviate this disparity by reducing the fine metallic silver to silver chloride, which is much more soluble in dilute cyanide solutions than metallic silver is.

Ores that contain antimony or tellurium (unless these elements are present in minor traces) must be treated (roasted) prior to being brought into contact with the cyanide solution.

In base metal ores—ores that contain base metals such as iron, lead, zinc, and copper—the loss of cyanide [cyanogen—$(CN)_2$] can be reduced significantly by leaching with very weak cyanide solutions. The affinity of cyanogen for gold and silver, regardless of its strength, is greater than its affinity for base metals. However, a weak cyanide solution tends to be much more selective in attacking gold and silver than a strong solution, which attacks available metal relatively indiscriminately. Lead and iron are for all practical purposes unaffected by weak cyanide solutions.

When gold is present along with copper and zinc in their metallic state, the solvent action of the cyanide on the free copper and zinc is practically nonexistent.

However, if the copper and zinc are in the form of oxides or carbonates, the reverse is true.

Potassium cyanide (KCN) is a compound of potassium, carbon, and nitrogen, consisting of one atom of each of these three elements per molecule. Potassium cyanide is extremely active with many metals. Gold potassium cyanide salt [$KAu(CN)_2$] is 68.3% gold; it is soluble in water. Silver potassium cyanide salt [$KAg(CN)_2$] is 54.2% silver; it is also soluble in water. In order to take place, the reaction of silver and gold with cyanide solutions must get oxygen from the air, or from hydrogen peroxide (H_2O_2), or from some other compound that will act as an oxidizer. Gold potassium cyanide solution, when evaporated, leaves octahedral crystals of gold potassium cyanide.

Oxygen is supplied from the water, by mechanical agitation, in compressed air blown up through the ore and solution, by sodium dioxide (NaO_2) or hydrogen peroxide, or by other oxidizers. Sodium dioxide reacts with the cyanide water solution to yield hydrogen peroxide, free oxygen, and sodium hydroxide.

Twenty to forty pounds of potassium cyanide is required to dissolve 1 lb. of gold from a free-milling gold ore. The time required to dissolve a given quantity of gold or silver from an ore depends on the strength of the solution and the amount of oxygen supplied. When a free-milling ore is being handled correctly, the best rate of solubility is usually accomplished with a 0.25% cyanide solution.

You can put together a miniature Pachuca tank to test an ore to determine its fitness for cyanide extraction. See Figure 10.5. With this setup, you can make numerous tests with roasted and unroasted ore and also work out your best solution percentages for a given ore. The key to making these tests useful is getting accurate weights for your sample ores and doing accurate testing of the potassium cyanide solutions for total cyanide before use and for loss of cyanide during percolating. Test for free cyanide (available cyanide) and do a metal content assay of the solution after percolation.

To test the cyanide solutions, you need two 50-cc burettes graduated in tenths of cubic centimeters, a 1000-cc graduate, a couple of 120-cc titrating dishes, and a stand for the burettes. See Figure 10.6.

The test for free cyanide in a solution is simple and quick. It is made by titrating a measured volume of the solution with a standard solution of silver nitrate. When a silver nitrate solution is added to a cyanide solution, a white silver cyanide [$Ag(CN)_2$] precipitate is formed (a white turbidity). If there is no free cyanide present, the turbidity remains. If there is free cyanide, the silver cyanide immediately redissolves. The end point of the titrating is reached when a permanent white precipitate of silver cyanide is produced.

To make standard silver nitrate solution, dissolve 13.07 g of silver nitrate in 1000cc of distilled water. To make potassium iodide reagent, mix a solution of 5% potassium iodide and 95% distilled water.

To test a cyanide solution for the percentage of free cyanide, start by taking a clean burette and filling it with about 25cc of the cyanide solution in question;

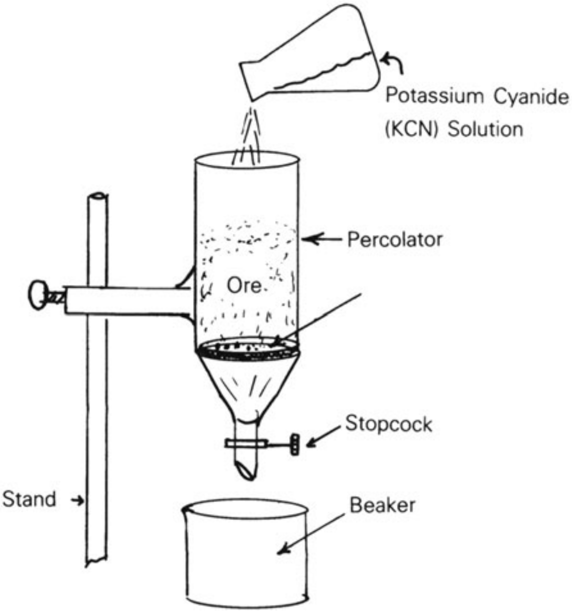


Figure 10.5. Cyanide extraction test setup

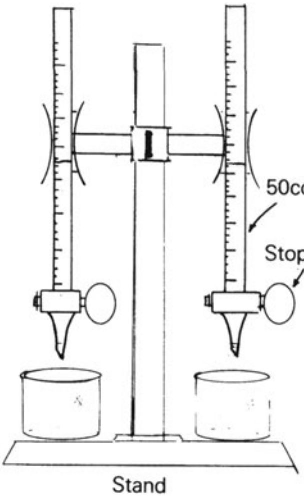


Figure 10.6. Burette setup for cyanide test

then close the stopcock. To fill the burette, do not suck the solution into the burette using your mouth; use a burette bulb. See Figure 10.7.

Tip the burette so that the solution is almost to the top end and slowly rotate it to wet down the inside of the barrel. See Figure 10.8.

Place the burette in the stand. Now put 25cc of your silver nitrate solution in the other burette, and tip and roll it as you did the cyanide solution. Place this burette in the stand and put a small beaker under the burette containing the cyanide solution. Now, with the burette, drop 10cc of the cyanide solution into the beaker. With a dropper, add two or three drops of your 5% solution of potassium iodide to the 10cc of cyanide solution in the beaker.

The purpose of the potassium iodide reagent is to make the precipitate formed (in the test) yellow in color, making it easier for you to see the end point.

Place the beaker under the burette containing the silver nitrate standard. Now cautiously, drop by drop, add the silver nitrate solution to the cyanide solution. Watch for a yellow turbidity (precipitate).

When the first precipitate (yellow) appears, stop the silver nitrate additions and shake the beaker; if the precipitate dissolves, add more silver nitrate until it reappears. Then stop again, and shake. The end point is reached when you have formed a permanent precipitate. When you have reached this point, check the number of cubic centimeters of silver nitrate that were required to reach the end point. Divide this number by 10 (the number of cubic centimeters of cyanide solution used in the test) to determine the percentage of free cyanide in the cyanide solution.

For example, if it took 7cc of silver nitrate to form a permanent precipitate in 10cc of cyanide solution, the percentage of free cyanide in the solution in question is 0.7%. The equation is

$$\frac{\text{7cc silver nitrate}}{\text{10cc cyanide solution}} = 0.7\%$$

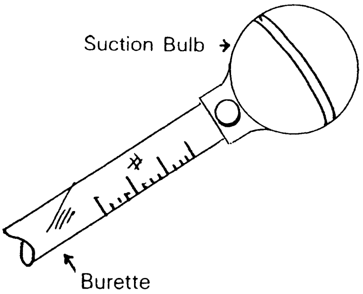


Figure 10.7. Suction bulb for burettes

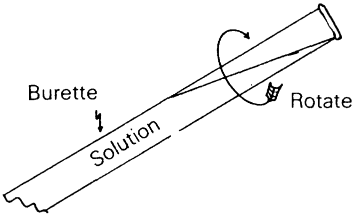


Figure 10.8. Wetting the burette

For strong cyanide solutions, take 10cc of the solution, add two or three drops of potassium iodide reagent, and dilute this volume to 100cc with distilled water. The number of cubic centimeters of silver nitrate standard required to form a permanent precipitate is equal to the percentage of free cyanide. See Figure 10.9.

To test a very weak solution for free cyanide, take 100cc of the solution in question and titrate this with the silver nitrate standard until you reach the end point. The percentage of free cyanide in the solution is equal to the number of cubic centimeters of silver nitrate required to reach the end point, divided by 100.

If it took 5cc of silver nitrate to reach the end point in 100cc of cyanide solution, you have 0.5% free cyanide.

You can purchase standard silver nitrate solutions or make your own. The amount of silver nitrate dissolved in a given amount of water does not matter as long as you know the percentage of your solution. My choice of 13.07 g per 1000cc of distilled water was to get the computations into easy, round figures. It takes two molecules of KCN to produce the necessary CN ions to unite with the silver ion from one $AgNO_3$ molecule in the precipitate $Ag(CN)_2$. The relative weights of the two molecules are

$$AgNO_3 = 108 + 14 + 48 = 170,$$
$$2KCN = 78 + 24 + 28 = 130.$$

The test's end point is best observed against a black background, as shown in Figure 10.10.

When potassium cyanide (KCN) is treated with dilute acid, hydrocyanic acid (HCN) is evolved. If this is done in a distilling flask, the hydrocyanic acid is distilled out and can be collected with an excess of sodium hydroxide in the form of sodium cyanide (NaCN). The sodium cyanide can then be titrated with silver nitrate solution to determine the total cyanide. See Figure 10.11.

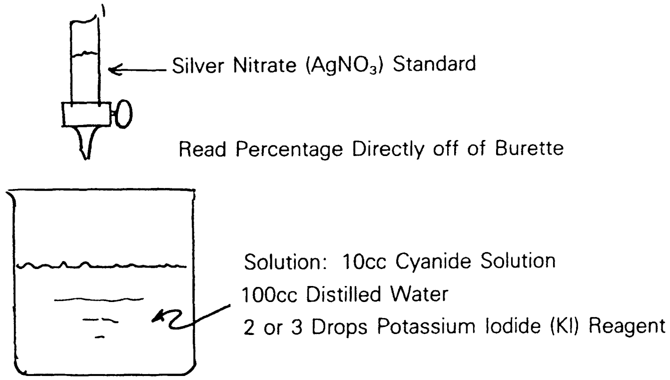


Figure 10.9. Solution for direct-reading cyanide test

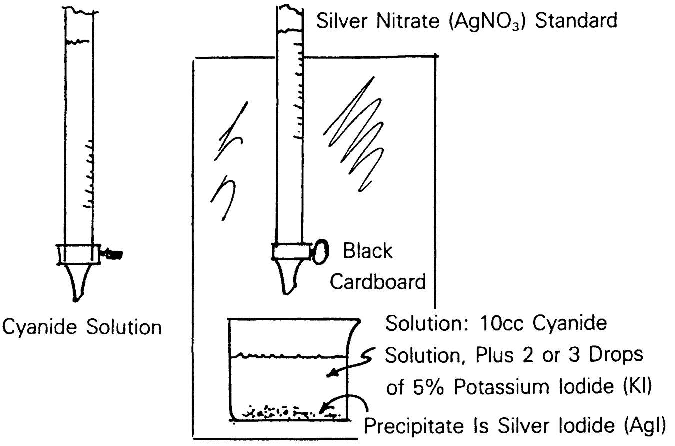


Figure 10.10. Testing cyanide with potassium iodide

To assay a cyanide solution for gold and silver values, take about ½ L of the cyanide solution and carefully evaporate it down to crystals in an iron evaporating dish. Stir constantly during the evaporation, working the sides down until everything is reduced to a small bulk. Do not evaporate to dryness; some moisture is harmless. Now, in the evaporation dish, add to the first evaporation 40 g of litharge (PbO). Mix this in well and carefully evaporate the material to dryness.

Transfer the contents—the litharge and metal salts—to a clay assay crucible, and add 15 g of borax glass, 5 g of bicarbonate of soda, and 2 g of argol or wheat flour. Cover this with a little borax glass and fuse it in the assay furnace at a red heat. When everything is quiet, pour the fusion into a cast-iron cone mold. Break away the slag and square up the lead fusion into a rough cube.

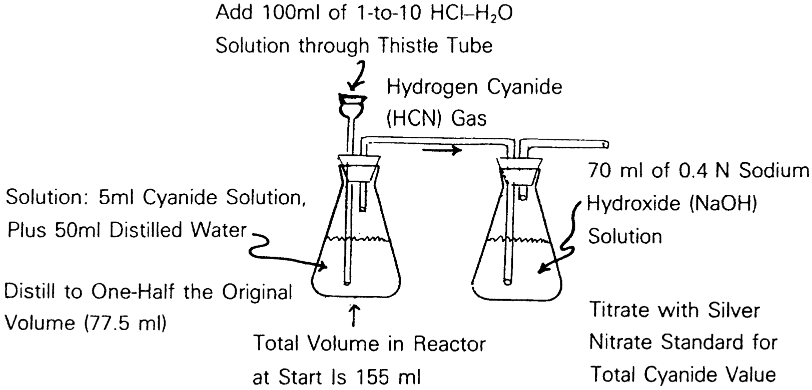


Figure 10.11. Test for determining total cyanide in solution

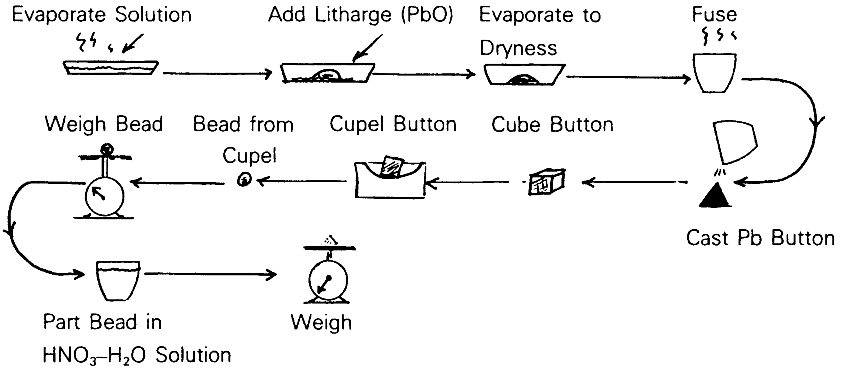


Figure 10.12. Flowchart for fire-assaying a cyanide solution for values

Cupel the lead fusion in a bone ash cupel, in the presence of oxygen. The resulting bead is the gold and silver. Weigh the bead, separate the silver with 1-to-1 nitric acid and water solution, and weigh the gold. The difference between the first and second weights is the weight of the silver. See Figure 10.12.

You can, if you choose, take your solution and very carefully evaporate it to dryness in a small tray made of pure lead; then fold the tray up and scorify it in a scorification dish. The resulting button is cubed, cupeled, and parted as usual. See Figure 10.13.

Cyanicides are any acids, soluble metal salts, or other substances in an ore that will destroy cyanide, leaving insufficient free cyanide to compound with the gold and silver. Any body of ore tailings or other material should be tested to

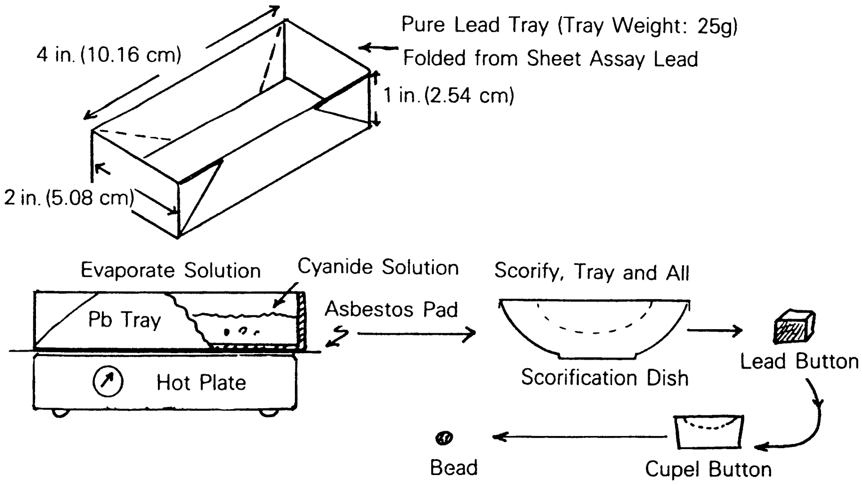


Figure 10.13. Scorification assay of a cyanide solution for values

determine how much caustic soda has to be added per ton of ore to neutralize these cyanide-consuming cyanicides.

To do the test, place 14.5 g of finely ground ore in 250cc of distilled water, and shake the solution for 10 min. Then with a burette filled with a standard solution of sodium hydroxide (NaOH), titrate the solution until it becomes neutral to litmus. The number of cubic centimeters of caustic soda required to neutralize the acidity of 250cc of wash water is multiplied by 0.1. This equals the number of pounds of caustic soda that must be added to each ton of ore in order to neutralize the acidic cyanicides.

For example, if 10cc of your standard sodium hydroxide solution were required to neutralize the 250cc aqueous solution, you would need 1 lb. of caustic soda per ton of ore to be refined: 10 × 0.1 = 1.0 lb.

One of the problems with cyanide solutions, especially if they are weak, is in getting them to exchange readily their gold and silver for zinc. In some cases a test with zinc will show that the solution is almost barren of value; only later do you find out that the solution is quite rich, but simply not reacting with the zinc.

The trick is to bring the solution to a point at which you get a satisfactory precipitation. The recovery of values should be at least 85%, and upward of 95% under excellent conditions.

Your first move is to assay the solution for values in grams of combined gold and silver per liter of solution (or ounces per ton of solution).

Assemble the setup shown in Figure 10.14. It consists of a 1-in.-inside diameter

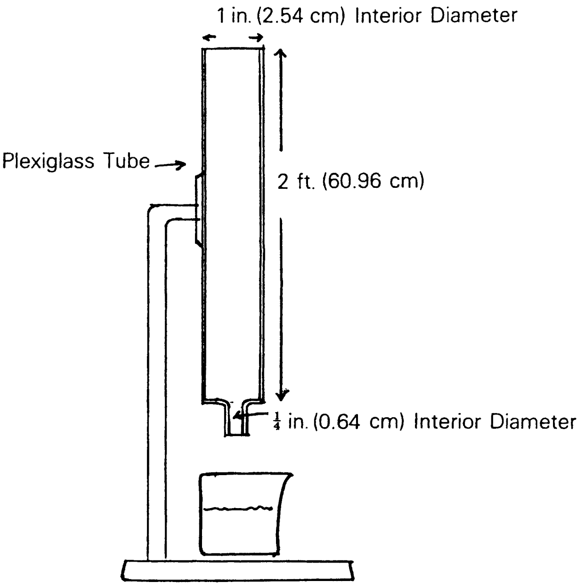


Figure 10.14. Test stand for checking ion exchange

clear plexiglass tube that is 2 ft long, supported by a stand in a vertical position. The bottom end is terminated by a short length of ¼-in.-diameter plexiglass tube, with sufficient room under the bottom end for a beaker. The stand can be made of wood equipped with a clamp to hold the tube and to provide for its easy removal.

Imagine that you have assayed, by one or another method, ½ L of your pregnant cyanide solution and established a bench mark for silver-gold content. Pack the plexiglass tube carefully with fresh zinc shavings to within 6 in. of its top. Now take a fresh ½ L of pregnant cyanide solution and pour it slowly down through the zinc shavings, catching it in a beaker.

Look closely at the zinc shavings in the plexiglass tube. If the precipitation is taking place properly, the gold should be deposited as a dark metallic covering on the shavings in the top of the zinc column, and the color in the tube should taper down from black to gray. See Figure 10.15. If the color is more or less reversed, as in Figure 10.16, it indicates that conditions are unfavorable for good precipitation.

Now assay the solutions from both tests and compare the results against each other. If your precipitation, like the one in Figure 10.16, is unsatisfactory, then you can pass the solution through two or three tubes and examine the color distribution.

The problem of unsatisfactory precipitation can usually be corrected by increasing the length of zinc-filled tubing the solution must travel through. In some

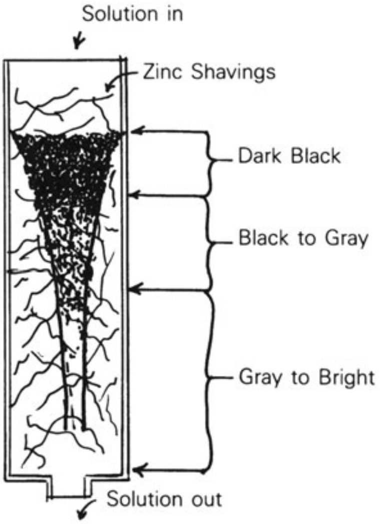


Figure 10.15. Checking cyanide solution with zinc: conditions very good

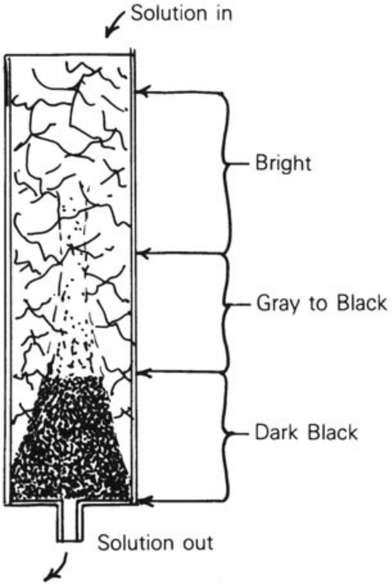


Figure 10.16. Checking cyanide solution with zinc: conditions bad

cases, an addition of KCN to increase the strength of the solution will do the trick. Your determination of the appropriate corrective measures must take into account all the factors raised by your tests. Make certain that you have done sufficient assays before and after a zinc pass.

The necessary cyanide contact time for a complete extraction will depend largely on the fineness of the gold, whether it is free or combined, and the presence and amounts of interfering substances (cyanicides). You can determine these things by setting up a series of small leach tubes, each with the same amount of ore, and testing with various strengths of cyanide and contact times. You can soon establish the correct solution, dwell time, and leach time for a given ore.

Cyanide is extremely toxic, as I have stated several times in this volume; however, the solutions used in leaching are so dilute that the amount of hydrocyanic acid (gas) given off is of little consequence if you have sufficient ventilation.

If you test the ore properly for acid content and acid-bearing salts, and add the necessary amount of caustic material to neutralize the ore effectively prior to leaching, your process should produce little or no hydrocyanic acid.

There is great danger of absorption through the skin when handling cyanide salts during the production of cyanide solutions; it is very foolhardy to do this without wearing protective clothing, gloves, and respirators. In fact, the system should be designed so that you are never required to come in contact with solid cyanide or cyanide solutions. Any work with cyanide should be done in a well-ventilated area.

When you consider how extensive the use of cyanide is, it is really amazing how few cyanide accidents occur. Perhaps this is the result of operators recognizing a very simple rule: *You do not take chances with potassium cyanide or sodium cyanide.*

One very dangerous part of a cyanide operation is the treatment of slimes from the zinc precipitation to dissolve the unused (uncombined) free zinc. Even after extensive washing, these slimes still bear some insoluble cyanide; when the slimes are then washed with dilute sulphuric acid, the remaining cyanide generates hydrocyanic acid gas. This part of the operation should be done in a well-exhausted reaction chamber built for that purpose; if you do not have this equipment, wear a respirator, even when working under a hood.

Another dangerous substance, about which there has been little discussion, is arsenic. Arsenic is usually soluble in cyanide solutions. If an ore contains appreciable amounts of soluble arsenic, the arsenic is precipitated with the gold and silver values onto the zinc.

When the slimes are treated with the sulphuric acid solution, they generate a very deadly poison gas, arseniuretted hydrogen. This gas is similar in toxicity to arsine (AsH_3)—a poison gas used in chemical weaponry, for which human beings have a tolerance of only 0.05 PPM (parts per million) in air. If inhaled, arseniuretted hydrogen passes from the lungs into the bloodstream very rapidly.

To repeat, slimes should only be treated in a closed chamber with good draft, and the acid solution should be added from the outside through a one-way trap.

Some people are much more susceptible to the effects of cyanide than others; they should not get involved at all with cyanides. If you are working with cyanide solutions (including cyanide plating solutions) and develop a headache, faintness, or dizziness, leave the area at once, go out into the fresh air, and do some deep breathing.

In case of internal poisoning, call a physician at once. An emetic or physical means should be used to induce vomiting.

In case of accidents, it is well to remember that hydrogen peroxide (H_2O_2) is a powerful antidote for cyanide poisoning. Hypodermic injections of solutions containing from 2% to 3% hydrogen peroxide have been used successfully, especially when injected at different parts of the body, at the same time that the stomach was being washed out with a 2% solution of hydrogen peroxide. Hydrogen peroxide combines with hydrocyanic acid (HCN) to form oxanide ($CONH_2$), a harmless compound; thus, $2HCN + H_2O_2 = 2CONH_2$.

The Vat Process

The vat process is simply an enlargement of the assay procedure in which gold values are reduced to gold chloride by sending chlorine gas up through the dampened ore. It is also related to the barrel process. The system is quite simple, and the following brief description should enable you to construct and operate a workable chlorine gold-extraction vat.

The ore is crushed, roasted, and moistened. The moistened ore is charged into the vats. The vats were formerly constructed out of wood but these have been replaced by various plastic and fiberglass tanks. See Figure 10.17. The vat is covered and the cover luted with clay to prevent any chlorine gas from escaping.

The gas from a chlorine generator or from bottled chlorine is introduced below the filter through a lead or plastic pipe. The gas flow is maintained until the gas has passed through the entire mass of ore in the vat and has dissolved the gold. The time required is established by experimentation. When this point is reached, the gas flow is discontinued, the top of the vat is opened, and water is poured over the ore until it is completely covered. The chlorine-charged water is then drawn off at the bottom and delivered to a holding tank. This part of the operation is called "precipitating the vat."

As solution is drawn off at the bottom, fresh water is added at the top until the solution coming off the bottom does not contain any dissolved gold chloride. This is determined by putting samples of the solution being taken from the bottom of the vat in a small beaker and adding a few cubic centimeters of copperas solution to them. If the solution turns black or brown, it is still carrying gold. The tailings are discharged, and the next batch is charged.

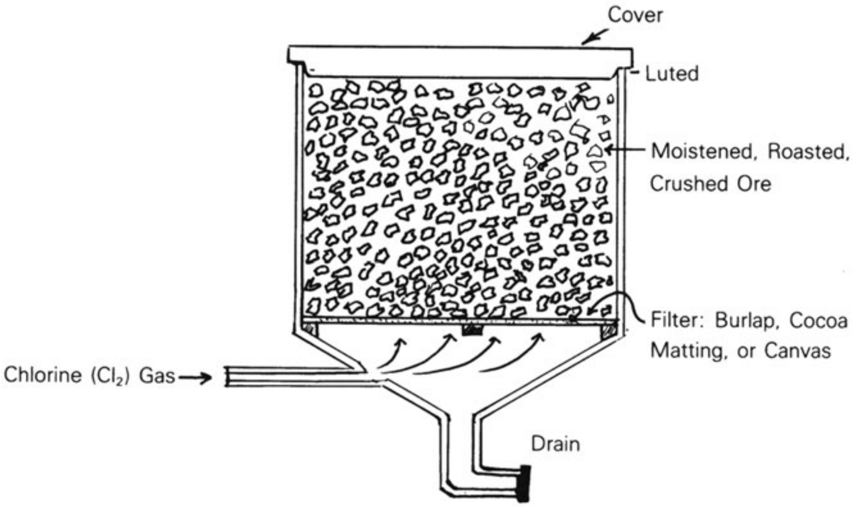


Figure 10.17. Basic chlorinating vat

The solution drawn from the vat is relieved of its gold content by precipitation with copperas or sulphur dioxide gas.

The chlorine generator, for making your own chlorine gas, is made of lead. Sodium chloride, manganese dioxide, and water are placed in the reactor; from time to time, dilute sulphuric acid is added to keep the gas generating. See Figure 10.18.

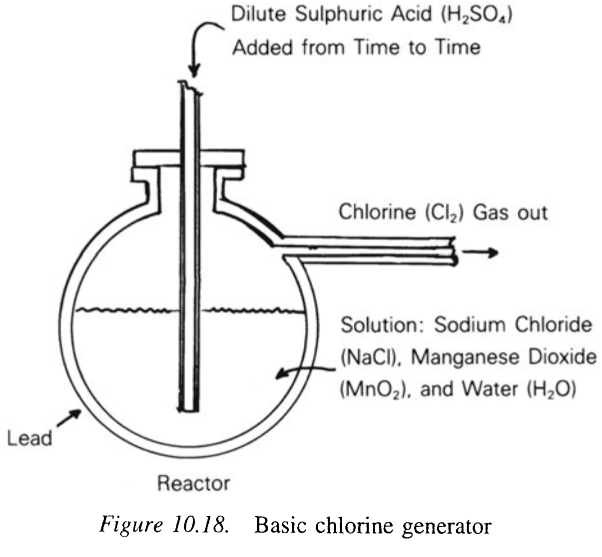


Figure 10.18. Basic chlorine generator

Refining Gold with Chlorine

Using chlorine to refine gold is simply a parting process for crude gold. The process is called the Miller process and is used when a gold doré bar is not fine enough to run in a gold cell and would require an excessive amount of fine gold to raise the gold percentage to a point at which it would be a good proposition for the Wohlwill cell. The Wohlwill cell requires a crude anode that is at least 90% pure gold. The problem is comparable to the one you encounter in the wet refining of 18kt green gold, with its high silver content.

The level of purity I am talking about is a bullion containing 80% to 82% gold and 17.5% to 19% silver, and a cyanidation bullion containing 73% to 75.5% gold and 20.5% to 23% silver. With bullion of this quality, the Miller process is usually the best way, if not the only way, to part the silver and gold economically.

The principle behind the Miller process is that, if chlorine is passed into a molten gold and silver alloy, the silver will be converted into silver chloride and will float on the molten gold where it can be bailed off. This, in turn, is premised on the fact that, unlike silver and certain other metals, gold does not combine with chlorine gas at elevated temperatures: Gold chloride ($AuCl_3$) decomposes at 254°C.

The parting is done in gas- or oil-fired crucible furnaces, in #18 French clay crucibles set inside #18 graphite guard pots. See Figure 10.19. The chlorine is supplied from 100-lb. cylinders and piped to the refinery from the chlorine house, a small building behind the furnace room. The chlorine is introduced into the molten bullion via a clay tube that is approximately 25 in. long with an inside diameter of 3/16 in. and an outside diameter of ½ in. See Figure 10.20.

The hydrostatic pressure of molten gold is about 10 lbs./ft of depth, and, as

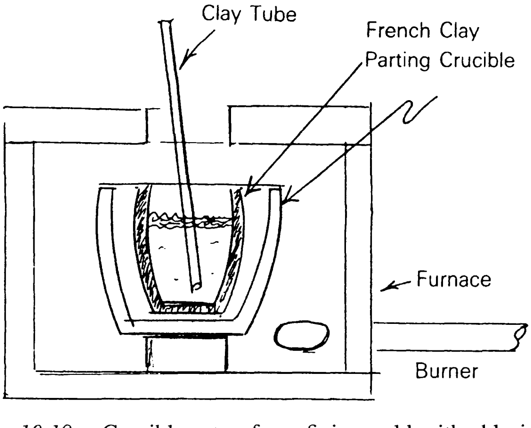


Figure 10.19. Crucible setup for refining gold with chlorine gas

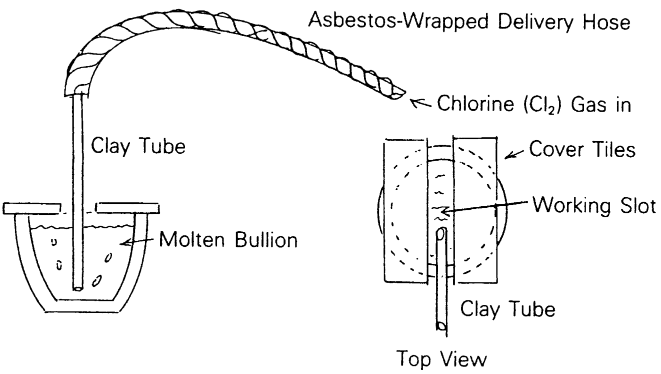


Figure 10.20. Chlorine delivery tube arrangement

the actual working depth is only about 6 in., the chlorine pressure (line pressure) needed is between 20 and 40 lbs./in.^{2} This makes for easy control.

The parting furnace is slowly preheated while the bullion is being melted in a standard crucible furnace. When everything is ready, the parting crucible, along with its guard pot, is carried to the bullion furnace and about 600 ounces of molten bullion is charged into the parting crucible, which is immediately returned to the parting furnace. The clay chlorine lance is lowered to a point just above the molten bullion and allowed to preheat for a few minutes. Then the chlorine cylinder's valve is turned to allow a very low rate of chlorine release and the tube is lowered into the bullion until it is approximately at the bottom.

The chlorine flow is increased gradually; and all of the gas released is absorbed by the bullion. Gold at its melting point will not combine with chlorine to form gold chloride; however, various other metals present in the bullion—such as copper and silver—will combine with the chlorine to form their respective chorides at the various heats of their formation.

The first metal to combine with chlorine is lead. It is then volatilized to white fumes. These are followed by the darker fumes of volatilized copper chloride. The first copper chloride volatilization that occurs is only partial, however. Soon after the first copper reaction, the liquid silver chloride starts to form. Because silver chloride occupies 2½ times the volume of silver, it must be removed from time to time. This is accomplished by bailing the silver chloride out of the parting crucible with a small, handled crucible and pouring it into shallow, cast-iron molds. The silver chloride is usually allowed to rise almost to the top of the parting crucible; then it is removed, a little borax flux is added, and the silver chloride is allowed to accumulate again.

The silver chloride is usually formed at a rate of about 1 ounce per minute. A 600- or 650-ounce bullion charge that is 20% silver will therefore take almost exactly 2 h (600-ounce charge) or slightly more than 2 h (2.16 h, 650-ounce charge) to be parted. The end point is verified by checking the color imparted to a clean cold clay tube held just above the gold. A certain brown stain on the tube tells the operator that the end point has been reached and that the parting is complete. This is not something I can describe: It has to be learned by repeated observation. The gold is cast into an anode and re-refined in an electrolytic cell. The anode as cast will be in the range of 99.3% to 99.5% pure gold.

For all practical purposes, members of the platinum metal group do not react with chlorine to form chlorides when subjected to the Miller process; therefore, they remain in the gold and are recovered as slimes in the electrorefining cell.

Chlorides formed in the Miller process are silver chloride ($2AgCl$), copper chloride ($2CuCl$), ferrous chloride ($FeCl_2$), ferric chloride ($2FeCl_3$), zinc chloride ($ZnCl_2$), and lead chloride ($PbCl_2$).

The silver chloride, previously parted off, is reduced to metallic silver, with soda ash used as a reduction flux. The silver, like the gold, is cast into one or more anodes for electrorefining.

Other Processes

The affinity of silver for zinc, leading to intermetallic compounds such as Ag_2Zn_3, is the basis of the Parks process, which I have already described in the context of lead collectors. The system is viable, whether carried out on a lab scale or with sweeps and residues amounting to tons of material.

Sulphur is a useful tool in the recovery of silver from intractable materials such as silver–tungsten alloys. The exothermic reaction of silver with sulphur forms silver sulphide (Ag_2S), effecting a parting.

Mattes, in metallurgical terminology, are solutions of metallic sulphides that have a lower melting point than the corresponding slags of the metals and are much denser than the corresponding slags. Because mattes are immiscible in both metallic and slag phases during smelting, they are often used for collecting metal values during smelting.

The Orford process is based on the extremely high affinity between nickel in its matte phase and copper in its matte phase. A slow cooling technique is used to crystallize a nickel–iron metallic-phase alloy from a matrix of copper, nickel, and iron matte.

The concentration of metals of the platinum group is extremely high in the nickel–iron metallic phase, which is due to the high affinity of the platinum-group metals for the nickel matte phase. This makes separation of the platinum-group metals from the crystalline nickel–iron alloy a simple magnetic separation proposition.

The Patterson process is rapidly replacing the Parks process as the most popular method for separation of silver values from lead. In this process, the lead is brought to a temperature of between 1000°F and 1050°F, and a small portion of zinc is added to it and rabbled in. The bath is allowed to cool slowly to a point at which a crust of silver–zinc forms. This crust is skimmed off.

The silver, lead, and zinc crust is charged into a zinc retort, and the zinc is distilled off. The residue in the retort is silver–lead, which is separated by cupellation.

In a conventional cupellation process, the material is melted in a shallow hearth reverberatory, and one or more jets of air are blown across the surface of the bath to oxidize the base metals (such as copper and lead), leaving the silver behind on the hearth in a sufficiently high state of purity to be cast into anodes for the Thum cell.

The cupellation process has not changed in hundreds of years, but there is extensive research today to try to improve the relative inefficiency and slowness of this very basic low-tech system of separation. Experiments are being conducted with such things as surface area (oxygen bath interface area), oxygen enrichment of the air jets (by means of pure bottled oxygen), pressure of the oxygen at interface, agitation of the bath, and sparging (lancing the oxygen into the bath with refractory pipes). The time of cupellation is said to be reduced by over 30% by sparging with crude air and over 60% by sparging with pure oxygen. The above methods of improvement are under study singly and in various combinations; much of the problem is in the physical aspect—sparging pipe construction, material, and so forth.

There has been some effort to develop a viable extractant that is highly selective. Polyether dibutyl carbitol, called DBC for short, is one of the many extractants under investigation. Using DBC as a solvent presents two main problems: a high loss of the solvent and a requirement that the solvent be of high purity. For the basic flowchart for DBC use, see Figure 10.21.

Many organic compounds containing oxygen atoms are capable of extracting precious metal values from acidic chloride solutions. The problem is to harness these chemical tendencies so that they will operate economically on a large scale.

The ferrous chloride ($FeCl_2$) system, as far as I have been able to determine, is still largely in the experimental stage, in relatively small reactors (no greater than 14 L in size). The typical charge consists of 4000 g of concentrate plus 977 g of ferrous chloride and 8 L of water. The contents of the reactor are agitated by vibration—external shaking or an internal impellor. The reactor is kept under a pressure of 40 lbs./in.^2 with pure oxygen, so the materials involved in the reaction are the concentrate, oxygen, ferrous chloride, and water.

Extraction rates of 99.1% to 99.7% for silver and 98.2% to 98.6% for copper are claimed, using this method. Reaction time for completion is about 4 h, with an oxygen consumption (by the reaction) of 300 g. The temperature is controlled at between 100°C and 115°C by cooling. The reaction is exothermic.

Of the sulphides in the concentrate I used when trying this method out, 65% reacted. Of this 65%, 94% were oxidized and 6% were converted to sulphate ions. Iron, antimony, and arsenic extraction registered at 0.1% or less. The iron was converted to insoluble oxides, and the arsenic present in the charge precipitated in the reactor as insoluble antimony oxide hydrate. See Figure 10.22.

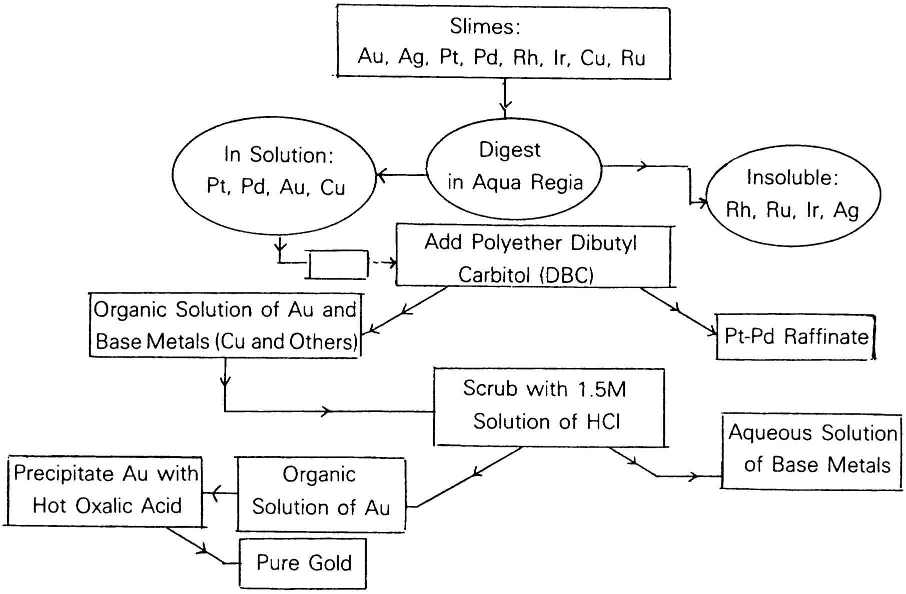


Figure 10.21. Flowchart for basic oxy-organic extraction

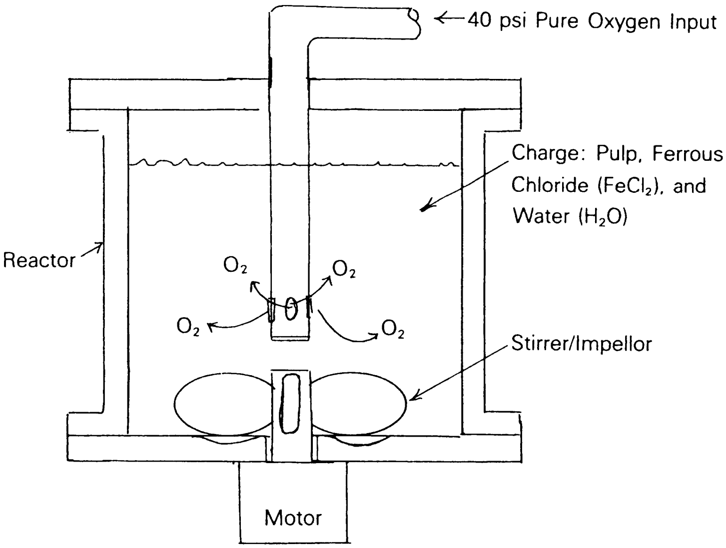
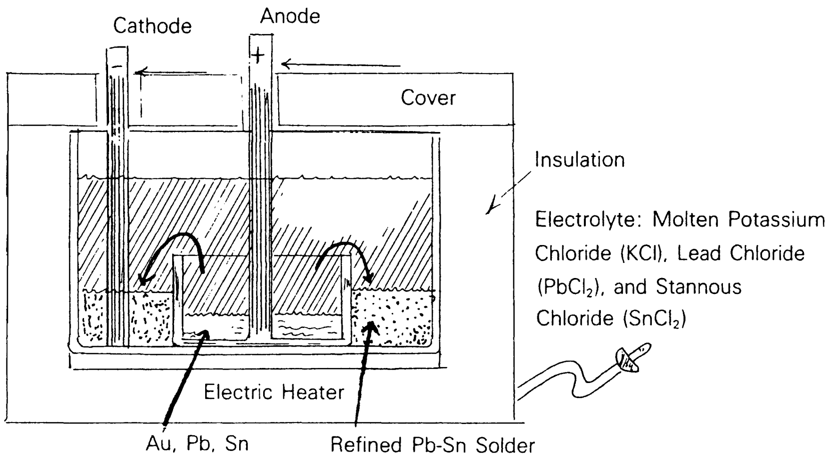


Figure 10.22. Basic setup for ferrous chloride–oxygen leaching



Cathode, Anode, and Anode Cup Are Tungsten

Figure 10.23. Basic setup for recovering gold from tin/lead solders

Research has been under way for 50 years to salvage gold from tin/lead solders, spatters, and scrap solder from the electronic industry. The gold is picked up by the solder during various soldering operations. Merely salvaging the gold from tin/lead solder is simple enough; however, doing it and then returning the solder to a form in which it can be easily refined and reused is a more difficult matter.

The Parks process does not work in this situation because the tin in the solder is soluble in the zinc, making the tin/lead recovery next to impossible.

Another method that has been tried is electrorefining with aqueous electrolysis, using an electrolyte containing fluosilicate compounds. Fluosilicate is a salt of fluosilicate acid (H_2SiF_6). Although the method results in tin/lead being deposited at the cathode and gold and silver remaining in the anode slime, the tin loss in the system is 20% of the original tin content of the crude starting anode.

E. K. Kleespies, J. P. Bennetts, and T. A. Henrie of the United States Bureau of Mines have worked out a system whereby the scrap solder can be refined by electrotransport in a molten chloride salt electrolyte. In this system, the refined solder is recovered at the cathode while the gold, along with copper and other impurities, remains at the anode. See Figure 10.23.

Recovery of Platinum and Palladium from Catalytic Converters

Although I have covered wet recovery of metals of the platinum group, I have said nothing thus far about extracting these values from the increasing collection of catalytic converters accumulating in junkyards and elsewhere.

The metallic composition of catalytic converters varies: Some are palladium, some are platinum, and some are platinum–palladium. Some operators advocate simply crushing the material up, boiling it in 1-to-3 hydrochloric acid and distilled water, washing the residue, soaking it in aqua regia for 72 h, filtering the solution, boiling off the nitric acid, diluting the thickened solution with water, precipitating metallic platinum (with ammonium chloride) and palladium (with potassium iodide or sodium chlorate), and converting each metal to sponge.

This method is widely circulated but is sketchy to say the least and much too costly to undertake without more definite information. Your first move should be to assay the material to determine exactly what you have.

You have basically three platinum metals with which to contend: platinum, palladium, and rhodium.

Catalytic converters usually take one of two forms: pellets that carry a deposit of platinum, palladium, or rhodium on a substrate of gamma alumina (a substrate is a substance whose reactivity is increased by means of a specific enzyme); or a monolith of some combination of platinum, rhodium, and palladium deposited on a honeycomb (usually made of a ceramic material) with a wash coat of gamma alumina.

Some converters are two way (those that oxidize carbon monoxide and hydrocarbons) and some are three way (those that, aside from oxidizing carbon monoxide and hydrocarbons, also remove nitrous oxides—"nox").

The effort required to get a good representative assay depends on the type of catalyst, whether it is fresh or spent, and other factors. Fresh catalysts can usually be decomposed with hot hydrochloric acid and chlorine, hydrogen peroxide, or sulphuric acid and phosphoric acid. Because the catalysts in the support media contain some silica, you have to use hydrofluoric acid to dissolve the silica. Platinum–rhenium catalysts are usually decomposed by heating the crushed material in dilute sulphuric acid that contains some sodium formate. The platinum, being insoluble in sulphuric acid and sodium formate, is filtered off, whereas the rhenium remains in solution in the filtrate. The platinum is then dissolved in aqua regia and precipitated with ammonium chloride.

The metallic element rhenium (Re) is a silver-white solid or a gray to black powder. In the powder form, it is flammable. It has a wide variety of uses—in flash bulbs, filaments, catalysts, high-temperature thermocouples, and as a material in metallic electroplating and vacuum vapor-phase depositing. Its principal source is molybdenite, but it is also recovered from refinery residues, flue dust, and copper ore treatment.

The bulk of the catalytic converters that you are likely to process are spent converters, and this material—whether in honeycomb or in pellet form—is usually about 95% by weight gangue (reaction by-products, carbon, organics, ceramics). The only practical way to deal with this melange of gangue is to incinerate it, burning the carbonous material to carbon dioxide. The incineration is then ground to a fine powder.

The collected ash (residue), after grinding, should be blended (mixed) in a suitable mixer, such as a "Y" blender. See Figure 10.24. The blender consists

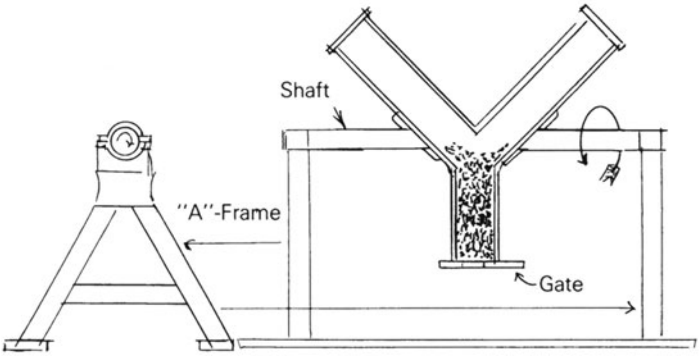


Figure 10.24. "Y" blender

of a Y-shaped plastic or metal tube that can be rotated. With each revolution of the tube, the material is split into the two arms of the Y, then reunited in the single leg.

If the material is not incinerated properly, leaving behind carbonous materials that have not been converted into carbon dioxide (CO_2), the excess carbon can cause reprecipitation of the values when you get to the dissolving stage of your process.

The next problem is how to concentrate the values in a suitable solvent. One consequence of incineration is that some of the palladium is converted to palladium oxide, a black, green, or amber solid that is resistant to chemical attack but must be reduced.

Many reducing agents easily reduce palladium oxide to metallic palladium. Sodium formate in a carbonate-buffered aqueous solution is a good one to use. The reduction is carried out at approximately 190°F, with the solution at a pH of 10. The reduced palladium is washed and filtered; then the residue from the incineration and the reduced palladium are extracted and refined in the usual wet chemical manner.

The above processes are carried out in the standard manner using expensive reagents. If your operation is not efficient enough to recover a very high percentage of the values, you may find that catalytic converters are a losing proposition. You should also be wary of auto wrecking firms, who frequently have a very inflated idea of the value of the converters. I have seen claims of from 1–3 ounces each of palladium and platinum recovered from 10 mixed converters. The best policy here is to buy the converter guts by the pound, based on an assay.

11

Black Sands

The presence of black sands can indicate the presence of precious metal values, but it can also be a false alarm. There are far more barren black sands than black sands carrying values.

Black sands are basically composed of black iron oxide (magnetite) and iron titanium oxide (ilmenite), which look almost the same. Along with the magnetite and ilmenite are a dozen or more less common materials in various combinations and concentrations. Magnetite is easily removed magnetically, but ilmenite is only slightly magnetic.

Components of Black Sand

Magnetite (magnetic iron ore), SG 5.18

Ilmenite (titanic oxide), SG 4.5

Pyrite (FeS_2), SG 4.9–5.2
Marcasite [Missouri pyrite (FeS)], SG 4.8–4.9
Monazite (a rare-earth phosphate), SG 4.9–5.0
Rutile (TiO_2), SG 4.3
Scheelite ($CaWO_4$), SG 6.12
Tourmaline (a complex borosilicate of aluminum)
Wolframite [$(FeMn)WO_4$], SG 7.0–7.5
Zircon ($ZrSiO_4$), SG 4.68
Chromite (chromic oxide), SG 4.6
Chromium (CR), SG 6.92
Other Heavy Minerals

SG = Specific Gravity

Each aggregate can also be carried out further. For example, you could chlorinate the pyrite and produce sulphur, copper, gold, silver, and zinc. The remainder would be sintered iron oxide (Fe_2O_3), which could be reduced to pig iron in a blast furnace. In fact, this is a common practice in Japan.

Now, consider the specific gravities of the various aggregates: They range from 4.3 for rutile to 7.5 for wolframite, and many are quite close to each other. This makes separating each constituent material, by elutriation or some other means, extremely difficult. A wide array of machines, equipment, and processes have been created for the recovery of gold, platinum, and gemstones from black sand. None has been entirely successful.

The general rule is that inland placer black sand is much more apt to carry values than black sand found with beach sand. You can sometimes find gravels that will yield over 100 lbs. of black sand per yard of material. However, the presence of large percentages of black sand in gravels does not necessarily mean that you have hit the mother lode. As often as not, gravels carrying only minor amounts of black sand will be rich in values and worth working.

There are numerous ways to concentrate black sands—jigging, sluicing, tabling, panning by hand, or using one of the various mechanical types of pans. When going through black sands to retrieve the free gold and platinum, you must remember that these values are most commonly in a form resembling fine, thin fish scales. These are hard to trap and tend to float away. Always wet down the material thoroughly prior to trying for a recovery.

Sluices and Rug Mills

Unless you get sufficient riffling (frothing action) at the leading edge of each of the perforations in your sluice or rug mill, you will get poor or no separation, and the heavy material will go to the tails. The slurry must swirl upward and back when it reaches the leading edge, causing the material to rise high enough and fall far enough back to drop the heavy material and yet wash the light material forward on the next wave before it has a chance to sink very far. The height that the material is thrown upward and back is critical: If this were adjusted to perfection, you would need only one riffle to catch all the precious metal values.

When the material being carried in water down the sluice hits an obstruction, riffle, or pocket, it is deflected upward and backward. Now, when the material is thrown backward against the current flow, it must come to a dead stop or standstill before it starts forward again with the flow. It is during this microsecond, when the particles are at a dead standstill in equilibrium between the momentum of their backward deflection and their normal forward travel, that the separation takes place.

At the dead stop point, all of the material starts to fall downward, the heavier material falling faster than the light. If the heavy material has had sufficient time to fall behind the riffle before the material starts forward again, you have it trapped where you want it. See Figure 11.1.

The light material must start forward again soon enough after its dead stop and downward drop to clear the top of the riffle, whereas the heavy material

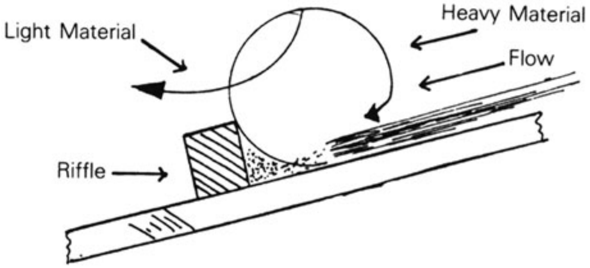


Figure 11.1. Riffle action: correct

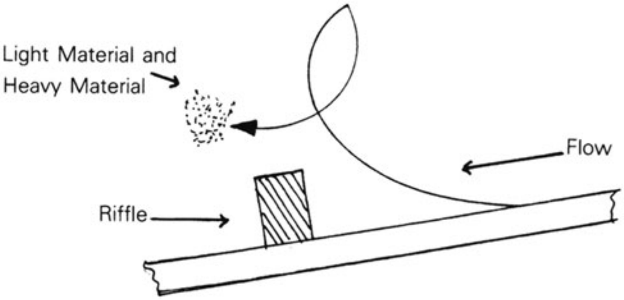


Figure 11.2. Riffle action: flow too fast

must sink far enough in the same time span that, when its forward movement resumes, it comes in contact with the face of the riffle member and is knocked down. If the flow is too great (fast) when the material is thrown up and back, it will all spiral over the riffle. See Figure 11.2. If the flow is too slow, the material will not separate and will sand up behind the riffle with some of both the heavy and the light material boiling over the top in a very short time. The riffle will become completely sanded and inoperative, and everything will then go to the tails. See Figure 11.3.

The factors in getting an effective sluicing action include the angle of the sluice slope, the speed of the flow, the height of the riffles, the spacing of the

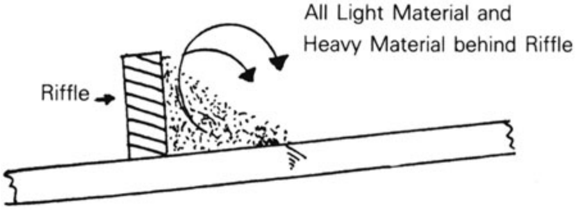


Figure 11.3. A sanded riffle

riffles, and the particle size of the material. The easiest of these to adjust are slope and flow, and they work together. Remember that the water on the surface is traveling much faster than that along the bottom of the sluice.

When you pan, you throw the material upward and forward to get the light material to flow over the tip of the pan. This is what you want the sluice to do at each riffle. The only difference is that, with the pan, you stop between motions, shake sideways, and establish some equilibrium between tosses. When you have the lip of the pan in the water and move the pan backward or forward, you again come to a dead stop at the reverse point of your play. See Figure 11.4.

The material also does the same thing, although not at the same time. There are many different designs for sluices, with different shapes, numbers, sizes, and angles of riffles. Because projecting riffles and cavities cause the same action when set up correctly, the most important criterion for a design is whether it gets good separation, without sanding up, in actual operation.

It is almost impossible to get any concentration without proper classification. This is a major fault with trying to use only a single small device—a rocker or a sluice box with a so-called scalper or classifier attached to it. Another problem with using a small (3-ft-long or shorter) rug sluice or rug plant, whether it has raised riffles or a punched plate, is that it is going to lose a good percentage of the values. Especially in the recovery of very fine values in black sands, your sluice should be a minimum of 30 ft in length, in addition to being designed and adjusted to operate correctly.

If your rug sluice is running properly for fine face values, you should still be able to see rug even after 6–8 days of running. Another way to test the correctness of your setup is to clean out behind each riffle and weigh each heap of material separately. You should have 70% of the total weight of the trapped material at three adjacent riffles. When you have reached this point, your design is right, the pitch correct, the water flow is correct, and your recovery will be high. See Figure 11.5.

A ¼-in.-thick punch plate with square, staggered holes, bolted down tightly against a rug 30-ft long or longer works very well with little value to the tails. See Figure 11.6.

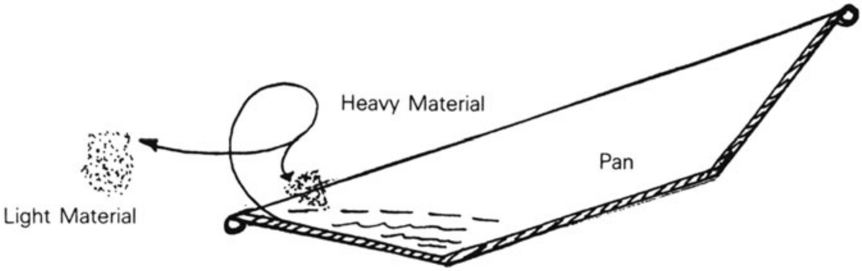


Figure 11.4. Gold pan action

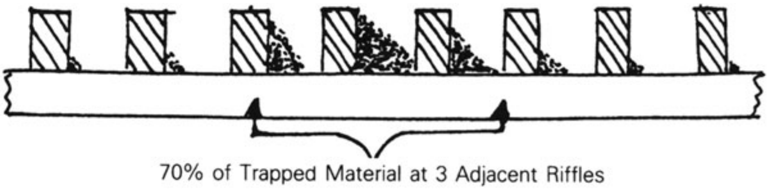


Figure 11.5. Correct riffle percentages for trapped material

A friend of mine was working some streams in Wyoming for gold with a little suction dredge of the type that floats on an inner tube. After working up and down a stream all day, with only a few gold flakes behind the riffles to show for their work, he and his partner headed back to camp. Next morning, they decided to clean up the dredge and give it another try. They took off the sucker hose, shook it out, and recovered 1½ an ounce of gold that had been caught in the hose. The spiral riffles on the inside of the hose had caught the values, which never even got to the scalper or sluice part of the rig.

They went out and bought 100 ft of 3-in. corrugated hose and resumed operations with this and the pump, water intake hose, Venturi tube, and sucking nozzle from the suction dredge. It worked fine, and they used the rest of the rig only to classify the material. The riffle and rug deck of the dredge were so short that had anything reached that part, it would have washed over, dumping the gold back into the river.

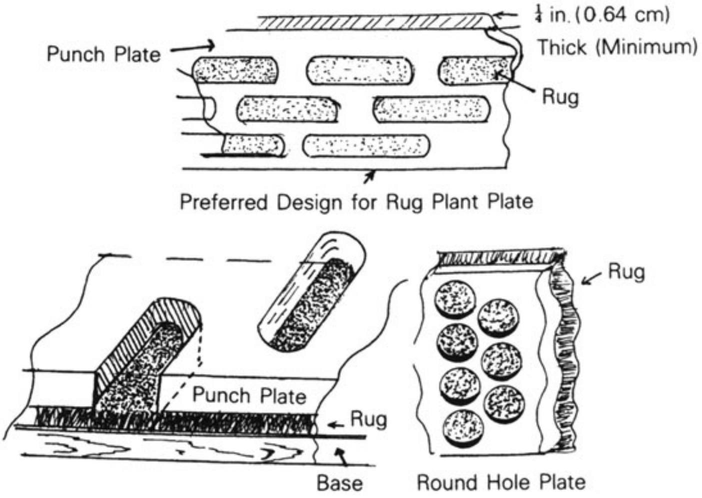


Figure 11.6. Rug plant arrangement

Refining Black Sands

The first step in refining black sands is to concentrate a portion of black sand from which you have removed, as completely as possible, the face values; then grind up a couple of spoonfuls (from which you have carefully removed the magnetics) in the mortar.

When performing a magnetic separation, cover your magnet's face with a thin piece of plastic (a plastic sandwich bag works well). Spread the dry, concentrated black sand out thinly on a board, and carefully go over it to remove the magnetics. In some cases, the values are coated with iron and will be carried over to the magnet, so you must examine what the magnet removes very carefully.

Wet Chemical Methods—Aqua Regia

Grind up a sample of the magnetics you removed with your magnet. This sample should be the same size as your nonmagnetics. Label them Magnetics #1 and Nonmagnetics #2. The other equipment and materials you will need are a small Pyrex beaker, an electric or gas burner, hydrochloric acid, nitric acid, a couple of test tubes, and stannous chloride or copperas (iron sulphate).

If you cannot obtain copperas, you can easily make it yourself. In a glass pie pan: Place a fist-sized chunk of steel wool or a handful of nails; carefully pour a solution of dilute sulphuric acid and water over this material—1 part acid to 15 parts (by volume) water. (When mixing acid and water, *never pour the water into the acid, always pour the acid very carefully into the water.*) This operation should be done outside or under a good draft hood. Wear rubber gloves, apron, and eye protection.

Dissolve the steel wool or nails in the dilute sulphuric acid (you might need to apply a little heat) and stir with a glass rod or stick. Fish out any particles that did not dissolve, place the liquid (which is now a solution of iron sulphate) out in the sun, and let it evaporate. You can evaporate it very carefully on the stove, but the sun is the best way. When the liquid has evaporated, yellow to yellow-green crystals of iron sulphate are formed. Scrape these dry crystals up and place them in a dry dark bottle labeled "Iron Sulphate ($FeSO_4 \cdot 7H_2O$). Low Toxicity."

If you cannot find stannous chloride, you can make it, too. Stir some shredded tin cans in a solution of 1 part hydrochloric acid to 15 parts (by volume) water. The bright coating on the tin can is the tin. When you see it strip, or go into solution, fish the remaining metal (iron) out to prevent it from forming iron chloride ($FeCl_2$) alongside your tin chloride ($SnCl_2$). The solution is then evaporated, leaving crystals of stannous chloride. These, when dried, should be bottled in a dark bottle labeled "Stannous Chloride ($SnCl_2 \cdot 2H_2O$)." If you have some pure tin metal to begin with, simply dissolve this in the hydrochloric acid solution

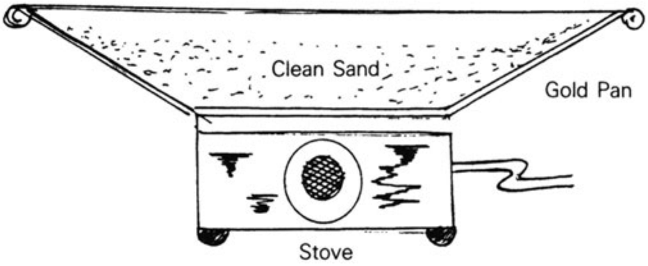


Figure 11.7. Sand bath

and evaporate to crystals. The crystals are either large and colorless or in the form of white flakes.

Return now to your black sand refining operation, and place a metal gold pan half-filled with dry white sand on your heat source. See Figure 11.7. Then place the beaker on the sand, heaping the sand around the base of the beaker. See Figure 11.8.

Mix, in a separate glass container, one part nitric acid and three parts (by volume) hydrochloric acid. When the two acids are mixed and slightly warmed, you have an orange-red liquid—aqua regia. This acid dissolves gold and platinum.

Once put together, aqua regia bubbles continuously, giving off gas. See Figure 11.9. Under no circumstances should you try to save aqua regia in a stoppered bottle: It will continue to convert to gas, and, when enough pressure has built up in the container, it will explode the container or blow its top. Only mix the quantity of aqua regia you need right away. Aqua regia does not dissolve silver, but it converts the exposed surface to silver chloride, stopping any further action.

Pour the aqua regia solution into the beakers, filling each beaker about one-quarter full. Turn on the heat and bring the aqua regia to a point just under

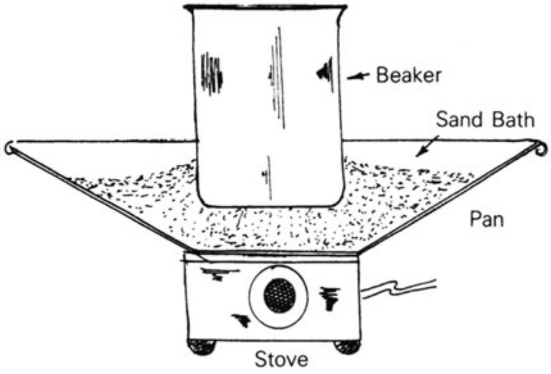


Figure 11.8. Heating with sand bath

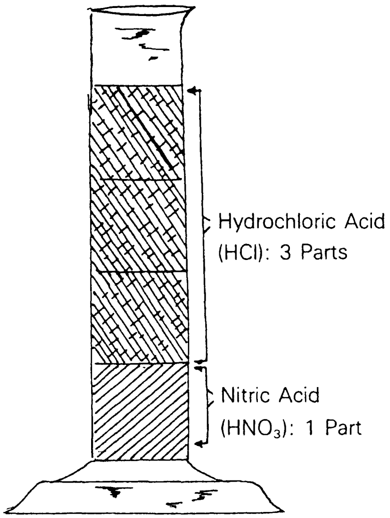


Figure 11.9. Aqua regia

boiling. Work outside or under the hood: Aqua regia is highly corrosive, and the fumes are *toxic.*

While the acid is hot, sprinkle slowly (while stirring the acid with a glass rod) some powdered nonmagnetics from your #2 sample. Add your #2 sample until between ½ and 1 in. of liquid remains over the black sand. Stir this material for 20 or 30 min. Boiling for hours is useless, because the values present are so finely divided that they—even the platinum—will go into solution quite readily. The brown fumes coming off the solution are mostly oxides of nitrogen, products of the interaction of nitric acid with various base metals. These fumes appear in numerous interactions of nitric acid with other substances.

Dilute the solution in the beaker with an equal amount of water and pour it through a filter paper in a glass or plastic funnel into a boiling flask. Coffee filters work fine, but you should use two together. See Figure 11.10.

Wash the sand residue on the filter with hot water, allowing the fluid to go into the flask containing the first liquid. The liquid in the flask is aqua regia with dissolved chlorides of gold and platinum, and of any base metals—such as tin and copper—that may have been dissolved. If any silver chloride is present, it will be caught on the filter. Transfer the aqua regia solution to an evaporating dish or shallow Pyrex pie pan. Place the dish on the sand in the gold pan. See Figure 11.11.

At this point, you want to get rid of the nitric acid in the aqua regia solution. This is done by heating the solution to evaporate the nitric acid. The boiling down and diluting process is repeated at least three times, each time progressively

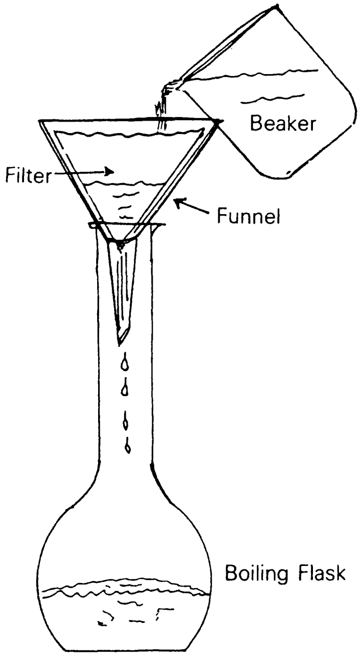


Figure 11.10. Filtering

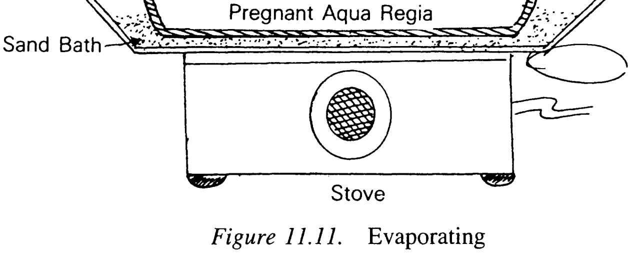


Figure 11.11. Evaporating

reducing the strength of the aqua regia until you are finally left with a simple solution of metal chlorides in aqueous solution.

This evaporation process to rid the solution of nitric acid is very crucial but not hard to do. Add to the solution in the dish a little full-strength sulphuric acid—½ ounce per quart of liquid is plenty. The purpose of the sulphuric acid is twofold: It hastens the expulsion of the nitric acid and it gets rid of any lead present in the solution. Put the heat on and work some sand up around the sides of the evaporating dish. Now boil the solution; if it sputters, reduce the temperature slightly so that you get just a gentle boil. Boil the solution down to a thick, syrupy consistency, add a little hydrochloric acid, and boil down again. This is the process you repeat three times.

If you boil the liquid down to a dry crust, you must add a few drops (no more) of a solution composed of a little sodium chlorate and warm water. First, you cover the crust with a few drops of full-strength hydrochloric acid; then you add a few drops of the sodium chlorate solution, one drop at a time, tilting the dish back and forth until the gold crust reconverts into a thick solution.

Warning: When you mix hydrochloric acid and sodium chlorate together, the solution releases an explosive gas, especially when cold. However, when the dish, the hydrochloric acid, and the sodium chlorate solution are all warm, very little gas is generated, presenting little or no hazard. As an alternative to adding sodium chlorate, you could add some nitric acid, but this would recreate aqua regia, defeating anything previously accomplished toward ridding the solution of nitric acid.

When you have boiled the solution down to a syrup-like consistency for the last time, turn off the heat and let the solution cool. Wash the sides of your evaporating dish with hot water. Now pour the syrup into a glass pitcher, washing it into the pitcher with hot water, and add hot water to the syrup in the pitcher until you have four times the volume originally in the pitcher. Let it sit or stand for at least 3 days.

If the solution contains any lead chloride or silver chloride, they will settle out as a white precipitate. Pour the clear solution into another clean glass pitcher, filtering the last part to catch the silver chloride and lead chloride. Save these. The solution should now be clear of any turbidity. If the solution contains mostly gold, its color will be yellowish brown. If it contains much copper or nickel, it will tend toward greenish brown.

Mix up 2 ounces of copperas (ferrous sulphate) in ½ cup of hot water. The copperas solution will be somewhat turbid, so add hydrochloric acid, drop by drop, while stirring, until it clears up. When the copperas solution is clear green, you are ready to proceed.

Pour the copperas solution into the dilute chloride solution (in the pitcher) while stirring with a glass or plastic rod. If gold is present in the solution, a brown cloud will form. This is your gold, in the form of a heavy brown powder. Let this settle overnight. See Figure 11.12.

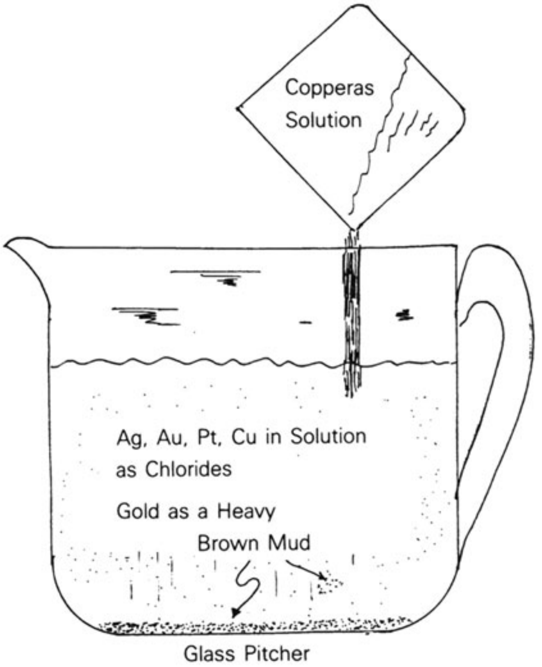


Figure 11.12. Adding copperas to precipitate gold

Now take some of the clear solution off of the top of the pitcher and put it in a test tube to a height of about 2 in. Warm this slightly and drop in a few grains of copperas. If you did not precipitate the gold entirely from your solution, a brown cloud will form around the copperas crystals. See Figure 11.13. If this is the case, you have to add more copperas solution to your pitcher. It takes about 1 lb. of copperas dissolved in 1 quart of hot water to precipitate 50 pennyweights of gold from a solution.

If you did not get rid of the free nitric acid in your boiling operations, the brown cloud formed in the solution will disappear (redissolve) in the solution.

To test the solution in the pitcher for nitric acid, put a small amount in a test tube and drop in a few crystals of copperas. If a brown cloud forms around the crystals and then disappears, you have failed to rid the solution of free nitric acid and you have what amounts to a pitcher full of mild aqua regia. If the concentration of nitric acid is high, you will have to go through the entire evaporation–dilution process with the contents of the pitcher. However, if there seems to be only a little remaining nitric acid, you can simply keep adding copperas solution until the solution in the pitcher stops releasing brown fumes and redissolving the brown cloud (gold), allowing the gold to settle to the bottom.

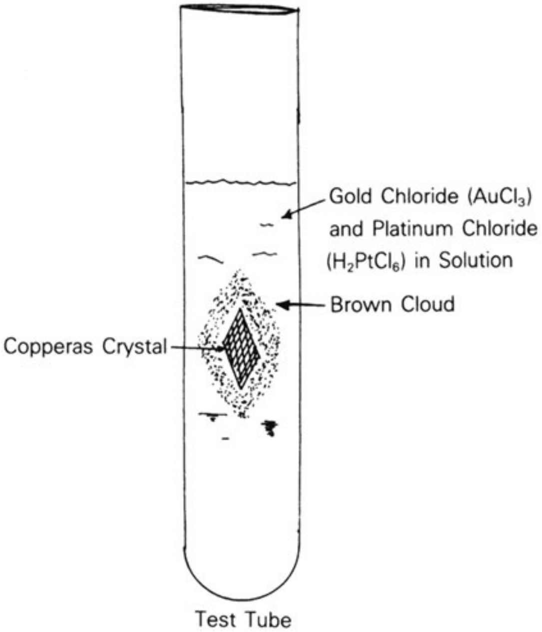


Figure 11.13. Testing the solution with a copperas crystal

The only real problem with this corrective measure is that if you were too far off with your initial evaporation, you could wind up with a huge bulk of liquid.

The settled gold will be mixed together with a yellow mud from the copperas, which you must remove. Pour off as much of the top liquid as you can; then pour off the rest, along with the gold and copperas mud, into a very clean Pyrex or glazed ceramic casserole dish. Cover the mud with full-strength hydrochloric acid and boil. This will dissolve the copperas mud but not the gold. See Figure 11.14.

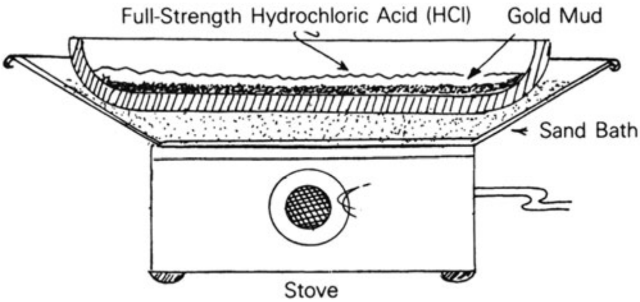


Figure 11.14. Cleaning precipitated gold of excess copperas

Wash the gold off onto a filter and run lots of hot water through it to get rid of the acid carrying the dissolved copperas mud. Now, set aside the gold on the filter to dry. See Figure 11.15. When dry, it can be melted down with a pinch of borax and should run 99.9% pure.

Thus far, you have crushed the nonmagnetics, put the values into solution, and precipitated the gold. This procedure should be carried out on a very small scale, with test tubes and very small evaporating dishes, using a Bunsen burner or propane torch, because you only are checking for the presence of values. From your findings, you can determine if the black sands are worth pursuing further. By carefully weighing the nonmagnetics initially and then weighing your recovery (if any), you have a very accurate wet assay from which you can determine the value per unit weight. Remember to count the weight of the magnetics removed from your original batch.

Of course, you can do a fire assay or have one done for you. I advise you, though, to run an assay for the presence of values before sending a sample for outside testing. Dry runs by an outside assayer cost just as much as tests that indicate rich samples. You are not looking at a very costly setup anyway, and it will pay for itself quickly.

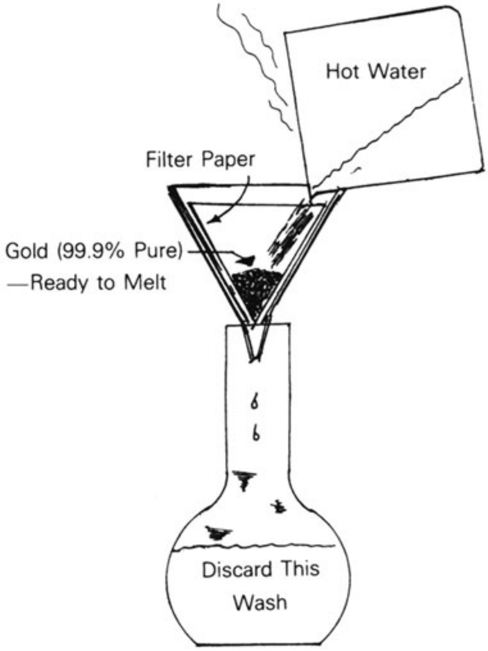


Figure 11.15. Washing gold powder

Wet Chemical Methods—Ammonium Chloride

You should now check the solution from your gold-extraction process for platinum. The most common chemical used to precipitate platinum from a platinum chloride solution (which is what you have) is ammonium chloride (NH_4Cl), more commonly known as sal ammoniac. It has many industrial uses aside from being a platinum precipitant: It is used in metallic soaps, batteries, and soldering fluxes, among other things.

A word here about ammonium chloride: If you buy a cheap grade to make up your solution, it is apt to produce a muddy solution that will have to be filtered prior to use: this is not the case with a good grade of ammonium chloride. Dissolve ½ ounce of good-grade ammonium chloride in ½ to 1 cup of water, and pour about half of this into the platinum chloride solution. Both solutions work faster if they are warm. Stir the combined solution well and let it settle. See Figure 11.16.

The precipitate, if platinum was in solution, is ammonium chloroplatinate, a bright orange powder.

Unlike gold, which completely precipitates as a brown powder, platinum will not entirely precipitate from solution under any circumstances. This is evident when you test a platinum chloride solution after precipitating the platinum: it will show the presence of residual platinum in solution. The quantity, however, is so minor as to have little or no value.

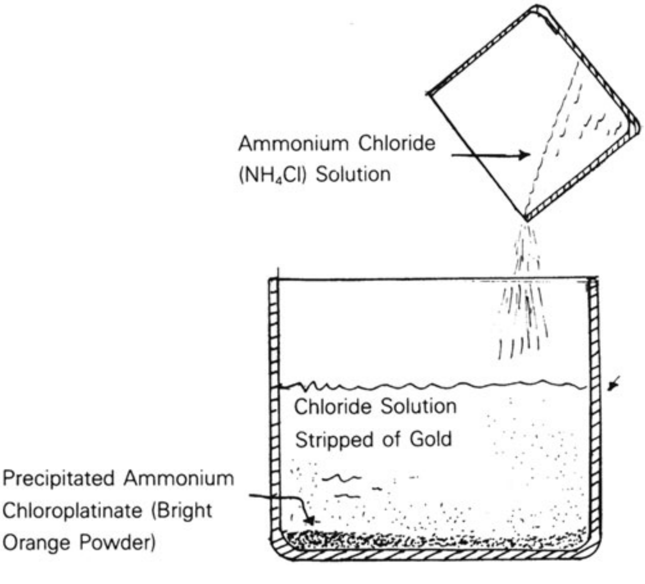


Figure 11.16. Precipitating platinum

Now, take the dry orange powder, which has been washed off onto a filter, and heat it strongly in a crucible over a Bunsen burner, propane burner, or stove. The ammonium chloride will decompose and go off as a fume. Work under the hood or outside, staying upwind from the fumes; do not breathe them because they are corrosive and dangerous to your lungs. See Figure 11.17.

Do not do this heating in your gold-melting furnace: it is too hot. All you want to do is drive off the ammonium chloride, leaving the platinum as a lump of gray metallic powder called platinum sponge. If the fumes coming off the material are white, your heat is correct; if they are black or yellow, your heat is too high, and you are losing platinum. Ammonium chloride sublimates (goes from solid to vapor without becoming liquid) at 350°C (662°F).

Now test a small quantity of the magnetics in your #1 sample (the magnetics you removed from your original sample) to see what quantity of values, if any, were picked up as magnetics. Of course, if the assay on the #2 sample came up black, do not waste time on #1.

The best way to learn how to master this very simple extractive procedure is to make up small samples of barren quartz, beach sand, or black sand, and add some gold and platinum filings to this barren sample. Then run through the entire process with these. By doing so, you will see what happens and what to expect. Time spent running these acquaintance experiments is very well spent.

I have now covered the basic recovery method for colloidal particles of gold and platinum, which is to put the metallic values into solution and precipitate them with reagents—in this case, two reagents: copperas (ferrous sulphate), to drop the gold out of solution, and ammonium chloride, to drop the platinum out of solution.

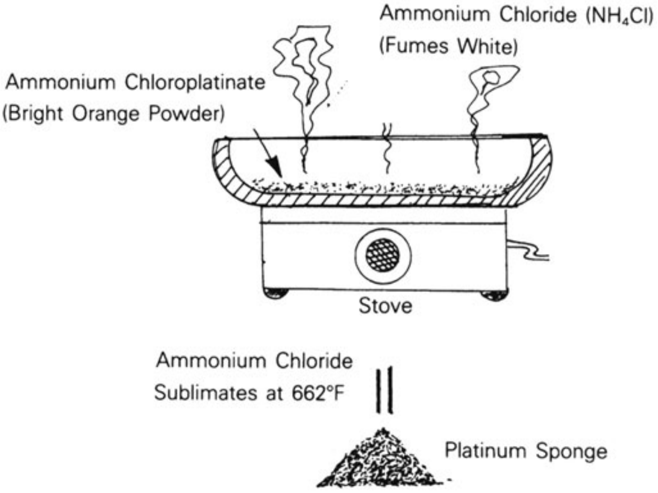


Figure 11.17. Reduction to platinum sponge

Wet Chemical Methods—Sodium Hydroxide

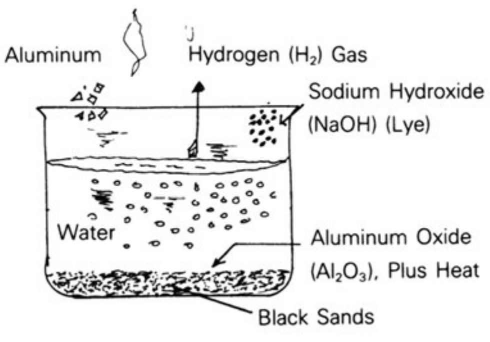
Take a fresh sample of black sand and wash it in a solution of hot lye (sodium hydroxide) and water. Sodium hydroxide is basically a by-product of chlorine production by the electrolysis of brine.

Lye can be purchased from your supermarket, but be careful that you do not buy a mixture of anhydrous lye and chips of aluminum. In this type of mixture, when wet, the lye reacts with the aluminum, reducing it to aluminum oxide and giving off hydrogen, an action that is accompanied by substantial heat generation. See Figure 11.18. You want plain lye.

When wet, lye is highly active and quite caustic: It can cause extensive damage to your skin. The chemical burn produced by lye is much more devastating than an acid burn; so use caution, wear protective clothing and eye shields, and avoid breathing the vapor. Never allow lye and water to come in contact with aluminum; their reaction is not only violent, but very explosive. Use plastic or glass containers.

Use a tablespoon of lye to 1 quart of water. Place this in a large glass bowl, add a few spoons of nonmagnetic crushed black sand, and stir it well. Pour off the liquid and repeat, until the discard liquid is fairly clean. You can add a dash of ammonium hydroxide to help clean the black sand and remove any patina (organic tarnish) on the metal values. This operation can be done before crushing, or after crushing, or both before and after. The object is to clean and brighten the values. You can also substitute hydrogen peroxide for ammonium hydroxide, which will provide oxygen to aid in the cleaning process. The operation can be done with a small tumbler or in a large Pyrex bowl with a wooden spoon.

Cleaning the black sand as described above, prior to extraction of the values with aqua regia, is unnecessary and a waste of time, chemicals, and effort. It is very useful, however, prior to mercury extraction or cyanide extraction.



Reaction: $3H_2O + Al_2 + NaOH = 3H_2 + Al_2O_3 + NaOH + Heat$

Figure 11.18. Cleaning black sands with sodium hydroxide

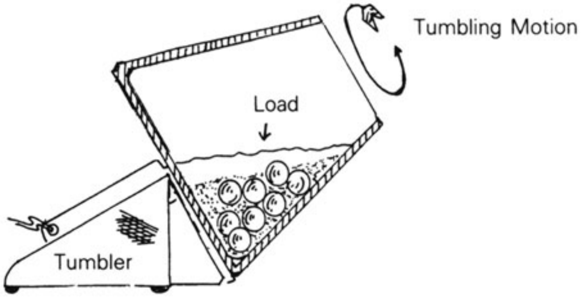


Figure 11.19. Ball tumbling

Mercury Extraction

Place clean, crushed black sand in a small tumbler with a touch of lye water, and add a couple of spoons of mercury and 10–15 (⅝–1 in. in diameter) clean, bright ball bearings. See Figure 11.19. When you buy the ball bearings, they are coated with an oil film. Be sure to remove this with lighter fluid or by washing in hot soapy lye water, and wipe the ball bearings with a paper towel. One volume of mercury will pick up approximately seven volumes of gold.

Tumble the material overnight. The steel balls will burnish the metal values, and they will easily form an amalgam with the mercury, leaving you with a mixture of steel balls, black sand, and mercury carrying the metal values.

The next step is to build a mercury slime recovery table. Build a shallow wooden box, 1 ft wide inside by 3 ft long and 3 in. deep, with a copper bottom. See Figure 11.20.

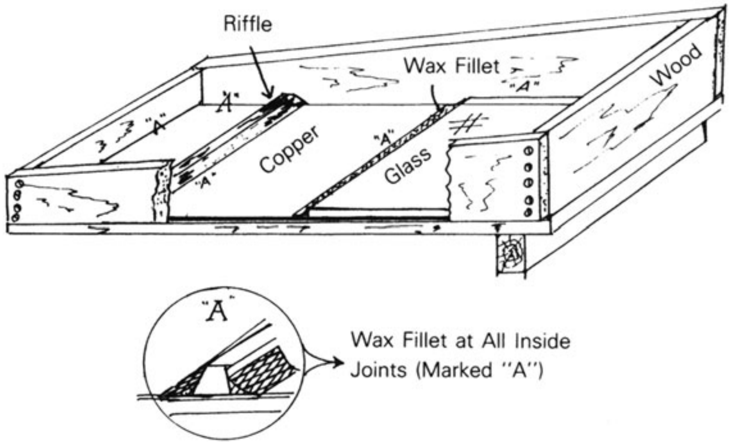


Figure 11.20. Mercury slime table

At one (interior) end of the box, place a sheet of glass so that it covers the copper plate for its entire width and for 8 in. of its length. Call this the top end. Three inches from the bottom end, across its width, attach a close-fitting riffle, ¼ in. in height. The riffle can be made of plastic or hard rubber, screwed to the bottom to make a close fit. All interior joints should be sealed with a candle wax fillet (concave strip).

Scrub the exposed copper, from the edge of the glass to the single riffle, until it is bright, using steel wool. Then rinse it clean and rubble it bright with a mild solution of potassium cyanide—½ g of potassium cyanide to 1 quart of distilled water. Do this with a mop consisting of a clean rag tied to a stick and then throw away the mop. Cyanide is a deadly chemical and produces a deadly cyanide gas when it comes in contact with an acid. Work outside, wearing rubber gloves. As an alternative, you could take your finished box over to a metal plating shop and have him swab the copper with a copper cyanide plating solution.

Wash the plate with hot distilled water, and then coat the copper between the edge of the glass and the riffle with mercury. You do this by putting a spoonful of distilled mercury in the center of the copper plate and, with a stiff glue brush, working it onto the entire surface of the plate in an even coat. See Figure 11.21.

You are now ready to use your recovery table. Set the table so that the top end is elevated by about 1 in. (a 3° to 4° incline). See Figure 11.22. Next, place some of the black sand and mercury mix on the upper end of the glass in a line

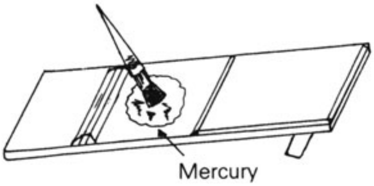


Figure 11.21. Distributing mercury over the copper plate

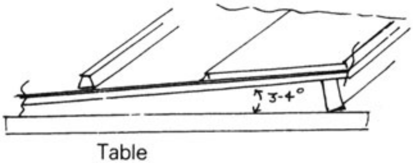


Figure 11.22. Inclination of the table

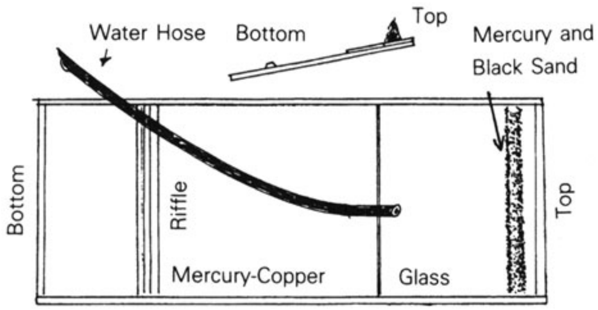


Figure 11.23. Placement of mercury–black sand mixture

going from side to side. See Figure 11.23. Of course, you remove the ball bearings, wipe them off to prevent rusting, and save them for the next run.

Now, with a ¼-in.-diameter rubber hose attached to the faucet, turn on the water so that you have a gentle stream of water. By directing the stream of water along the base of the line of black sand and mercury mix and moving the stream progressively upward with a back and forth movement, work (or flood) the material across and down the glass. See Figure 11.24.

As the material is washed downward, any free metal that escaped treatment with the mercury or was too large to amalgamate—and also some free platinum—is freely and easily spotted and can be recovered on the glass. By manipulating the hose and water flow, you can quickly isolate and capture these values.

When the fine material and mercury globules have descended onto the copper–mercury plate, the mercury carrying the values as an amalgam will attach itself to the plate, as will very fine values that escaped the mercury in the tumbler. The amalgam will build up on the copper–mercury plate. Meanwhile the black sand and some of the mercury will travel down and come to rest against the single riffle. At this point, the black sand can be washed over the riffle, as it will be floating on top of whatever mercury comes to rest at the base of the riffle. Afterward, this mercury can be retrieved with a rubber ear syringe. See Figure 11.25.

The rail at the lower end of your recovery table should be only a ¼ in. high to allow the water and spent sand to run off. See Figure 11.26.

The procedure is repeated until the copper–mercury plate shows sufficient buildup of amalgam. As the mercury becomes loaded with gold and other metals, it gets stiffer and stiffer. Do not let the material accumulate until it is too stiff to scrape off easily using a plastic windshield ice scraper. Occasionally, you should clean the plate of accumulated amalgam, setting this aside until enough is collected to make it worthwhile to retort off the mercury and recover the values. It is wise to add the mercury that you recovered from the base of the

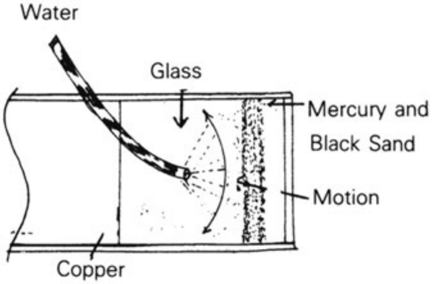


Figure 11.24. Working the material down the glass

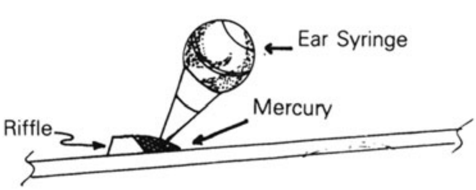


Figure 11.25. Retrieving the mercury

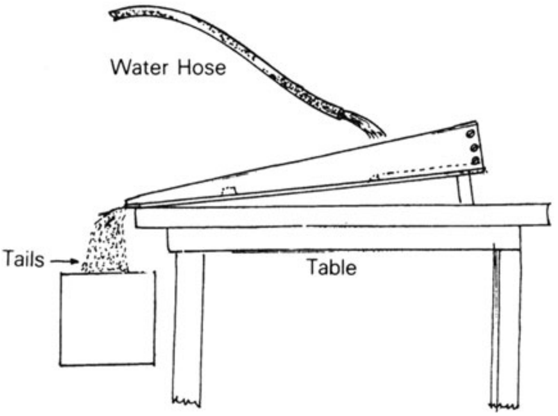


Figure 11.26. Runoff from the recovery table

riffle with the ear syringe to your cleaned up amalgam and retort it off at the same time. See Figure 11.27.

The material left behind in the retort is boiled in dilute nitric acid; the undissolved material (gold and platinum) is then washed and dried, and is ready to melt. When melting values extracted from a mercury amalgam that you retorted by vaporizing off the mercury, you should work under the hood. In the event that any mercury remained with the values (because of incomplete distillation),

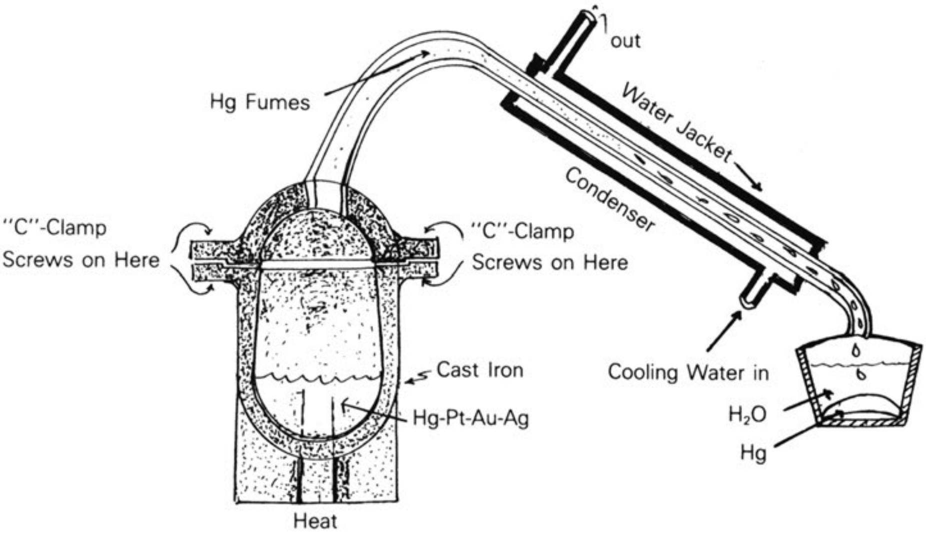


Figure 11.27. Retorting the mercury off

it surely will vaporize at the melting temperature of the values, and mercury vapor is very toxic.

Some authorities recommend separating the mercury from gold and platinum values by heating the amalgam in nitric acid, thereby putting the mercury into solution with the nitric acid as mercuric nitrate [mercury pernitrate—$Hg(NO_2)_2 \cdot H_2O$]. This does work; however, if any silver is present, you will have put the silver and mercury into solution together. No one advocating this method mentions the problems or additional operations required to separate the silver and recover the mercury.

If you dissolve the mercury amalgam in nitric acid, so that the gold and platinum sink to the bottom undissolved, what is the liquid? It is highly toxic (human beings have a tolerance of only 0.05 mg/m^3 of the compound in air), a very dangerous fire risk, and—in the presence of alcohol—produces mercury fulminate ($Hg(CNO)_2$], which explodes readily when dry and is used in blasting caps and detonators. Mercury is not entirely safe to handle or to retort under any circumstances, but dissolving it in nitric acid is exceptionally hazardous.

Mercury is also called quicksilver (hydrargyrum). It freezes at –38.85°C, boils at 356.6°C, has a specific gravity of 13.59, and is noncombustible. Its chief ore is cinnabar (HgS), which is mercury sulphide.

Mercury is highly toxic by absorption through the skin and by inhalation of fumes or vapors. It can be absorbed by the respiratory and intestinal tract. Inorganic compounds (amalgams) of mercury are highly toxic. When a mercury amalgam is left in moisture or water, it can be converted to methyl mercury by bacteria in the water. Methyl mercury is an extremely toxic material. Human beings have a tolerance of 0.01 mg/m^3 of methyl mercury in air, against 0.05 for mercury vapor alone. Human tolerance for alkali compounds of mercury is also 0.01 mg/m^3 in air.

Unfortunately, it is relatively easy to get into trouble with methyl mercury by spilling regular mercury. Spillage can create havoc due to mercury's droplet proliferation. Cleanup of any spillage, regardless of how minor, requires special care and must be complete.

As mercury has a vaporization point of between 671°F and 680°F, it is easy to separate from values by distilling. Home-made retorts, however, unless very carefully made on the basis of a good leak-proof design, are very dangerous. The same goes for mercury condensers. The old pipe and pipe cap home-brew retorts, along with the potato retort of the old prospectors, are excessively dangerous.

Purchase a commercial mercury retort and follow the directions carefully. The most common problems are using a retort that is improperly sealed (and leaks) and opening the retort too soon, with your nose in the path of the mercury fumes.

A more serious problem can result from having the discharge from the condenser immersed in water in the catch bowl. When the condenser starts to cool, a vacuum forms in the retort, drawing water into it, with a resulting explosion that under the right conditions is as violent as a hand grenade. Retorting at too high a temperature, with an insufficient water flow through the condenser can cause the mercury not to condense or to condense incompletely, resulting in mercury fumes discharging from the condenser.

Silver Values

If you use a mercury slime table to recover fine values, and these include silver, the silver particles will wind up in the retort along with the gold values; this material, when melted, will produce a gold and silver bar.

If you have decided instead to extract the values with aqua regia, it is advisable to take a pinch or two of your crushed black sands (at the point at which they are ready for aqua regia treatment) and cover them in a small evaporating dish with a solution of nitric acid and water—one part acid and one part water by volume. Bring this solution to a boil for a few minutes, dilute it with water, and pour the liquid through a filter. The black sand on the filter can be returned to the other black sands for treatment for gold and platinum. The filtered liquid will now be a silver nitrate solution, if any silver was present in the sample.

Look at the color; if it is greenish to dark bluish green, it is carrying other metallic nitrates, such as copper or nickel. Never mind about these. Divide the liquid about equally into two clean test tubes. To test tube #1, add five or six drops of hydrochloric acid. If silver is present in solution as a nitrate, it will precipitate as silver chloride, a white curdy mass. Run this off onto a filter and wash it with hot water until it is free of any lead chloride or other metal chlorides. When the white precipitate is placed in the sunlight, it will first turn light blue and then get darker and darker until it is black.

To test tube #2, add ammonium hydroxide (ammonia water), drop by drop, until the solution is changed from an acid to a base. When you reach this point, any iron present will drop out as a reddish brown precipitate.

Fire Assays

I have included in an appendix to this book a report of investigations on the assaying of black sands, by Paul Hopkins of the United States Bureau of Mines, which illustrates the process of fire assaying and points out the care required to arrive at a reasonably accurate figure. A quick, sloppy fire assay will do you no real good. The same goes for an atomic absorption (AA) assay; in fact, it can be even more confusing and misleading.

12

Fire Assaying

It is uncertain how old the process of fire assaying is. Procedures to perform a basic fire assay were published by Vannoccio Biringuccio in the sixteenth century. In most cases, it is used as a method of quantitative analysis of an ore—that is, to determine the amounts of gold, silver, and other values in the ore in ounces per ton. However, if your fire assay of an ore shows that it contains values that you did not previously know it contained, the process would be considered a qualitative analysis.

Various companies sell fire assay equipment, fluxes, and directions. Their usual pitch is that fire assaying is simple and fool proof. Some claim to have a universal flux suitable for all ores. This claim is simply untrue.

The fire assay is an extremely versatile tool; if properly done, it works well, but it takes great skill by the assayer and many years of experience. Because of the problems encountered even by a skilled assayer, a single assay means very little. The problem is not so much qualitative—even the sloppiest fire assay or scorification will indicate the presence of some values—as quantitative. A valid quantitative figure is very difficult to obtain.

The classical lead method of fire assaying, in which the lead quantitatively extracted and collected the various noble metals present is not clearly understood today. The mystery is even more clouded when it comes to ruthenium, osmium, and rhodium, as these elements are not very soluble in molten lead.

The object of the fire assay is to take a 29.166-g (1-assay-ton) sample of an ore and, using lead as a collector, to separate the precious metal values from the gangue by selectively dissolving them in the lead; then to separate the values as a group from the lead; then to separate the various values from one another by chemical means; and then to weigh them individually to establish their percent weights in the sample, which correspond exactly to their weights in ounces per ton of the ore being assayed. This is called the assay-ton system of fire assay.

One assay ton (A.T.) equals 29.166 g. Not all assays are done with samples weighing 1 A.T.; other commonly used multiples and divisions of the assay ton are 2 A.T. (58.332 g), ¼ A.T. (7.291 g), and ½ A.T. (14.583 g).

There are 29,166 troy ounces in one avoirdupois ton; therefore, if the bead recovered from a fire assay of an ore sample weighing 29.166 g (1 A.T.) weighs 1 mg (0.001 g), the ore in question contains 1 ounce of precious metal per ton. This is shown by the following proportion: 0.001 g/29.166 g ~ 1 ounce/ 29,166 ounces.

In a fire assay, there are seven basic steps to perform.

Step 1: Combining the material to be assayed with a suitable flux that includes a collector, such as litharge; and placing the assay and flux in a suitable crucible.

Step 2: Fusing the mixture in the crucible in an assay furnace to produce a metallic lead by the reduction of the litharge, which collects the precious metal values.

Step 3: Pouring the fusion into a conical-shaped cast-iron mold to produce a lead button or prill that contains the precious metals.

Step 4: Separating the lead button from the slag, and hammering the button into a cube.

Step 5: Cupeling the lead cube from the fusion in a bone ash cupel to oxidize the lead back to litharge, leaving behind in the cupel a bead composed of the precious metal values that were present in the assay sample.

Step 6: Parting the bead (separating the various values in the bead).

Step 7: Scorification, if necessary.

The first step is the crucial one. Unless you have the proper flux for the particular ore being assayed, you wind up with a undesirable conclusion: A lead button too large or too small to cupel properly. If the slag produced is too heavy (not fluid enough at assay temperatures), you can wind up with reduced lead particles—globules trapped in the slag. You can also wind up with a lead button that you cannot cupel back to litharge.

Fluxes

Most fluxes are made up of one or another combination and weight of the following components: sodium carbonate (Na_2CO_3) (also known as soda ash and sal soda), litharge (PbO) (lead monoxide), silica (SiO_2) (sand, quartz, flint), sodium tetraborate ($Na_2B_4O_7$) (borax), calcium fluoride (CaF_2) (fluorspar), wheat flour, potassium nitrate (KNO_3) (saltpeter), and potassium carbonate (K_2CO_3) (potash, pearlash).

The purpose of the flour (common household flour) is to reduce litharge to metallic lead, which collects metallic values. You can also use argol, sugar, or charcoal for this purpose. Flour is the most commonly used reducer when the nature of the ore is oxidizing or neutral.

When the nature of the ore is reducing, potassium nitrate is used (sulphide-bearing ores are reducing and silica-bearing ores are oxidizing). Potassium carbonate is used as a flux when major amounts of aluminum are in the ore or sample. In fusing chromate or chromite ores, hydrous potassium carbonate ($2K_2CO_3 \cdot 3H_2O$) is used in place of anhydrous potassium carbonate (K_2CO_3).

You want to combine the correct amount of correctly formulated flux and collector (litharge) with your ore sample, so that when the combination is fused, sufficient available litharge is reduced to create a lead button with a weight of approximately 28 g. A lead button of this weight will effectively collect the precious metal values that are present. At the same time, you want the flux to reduce the gangue to a slag that is easy to separate from the lead collector.

The ore sample can be reducing in nature, neutral in nature, or oxidizing in nature. If the ore is reducing in nature, the constituents of the ore sample will exert their reducing powers upon the litharge and reduce a percentage of it to lead. If the ore is oxidizing in nature, the opposite reaction will take place.

Without knowing the extent to which an ore is reducing or oxidizing, you would be hard pressed to come up with the correct formula and amount of flux and litharge for producing a lead button after reduction that weighs in the desired 28–30-g range. This weight of collector-lead button is necessary to collect the precious metal values that are contained in a 29.166-g sample (assay) effectively.

The first thing you need to establish is how much available deoxidizer (reducing material) to put in the flux, or how much oxidizer, in order to offset the oxidizing or reducing power of the ore itself, always leaving sufficient available reducing agent to reduce the remaining available litharge to a 28–30-g lead button.

This calculation is extremely easy if you have on hand an optical emission spectrograph, but for the purposes of this book I will assume that you do not. The alternative is to experiment.

Make up a charge (ore, flux, and litharge) without adding any materials of a reducing nature—such as flour, argol, or sugar. Next, add an excess of litharge to the charge; when you make the fusion, whatever elements are reducing in nature in the sample ore will reduce some of the excess litharge to metallic lead, producing a button. The weight of this button gives you a benchmark for the reductive power of the particular ore in question. Using the benchmark, you can formulate, reasonably accurately, the flux necessary to produce an optimum button after fusion. Remember that the reducing and oxidizing (redox) reactions occur simultaneously. You cannot have one without the other.

Suppose that your fusion with excess litharge and no added reducer produced no lead bead at all. This indicates that the sample either has no available reducer or an excess of oxidizer. Now suppose instead that your fusion produced a lead button weighing in excess of 30 g. This indicates that the sample contains excessive available reducer, requiring you to make up a flux that has just enough oxidizer (saltpeter) to lower the natural reducing power of the ore into the desired range.

The variables you need to fix are the amount of litharge to use, the amount of oxidizer to use, and the amount of reducer to use, based on the reducing or oxidizing power of the ore.

It is possible to have both natural reducers and natural oxidizers in the same ore. In such a case, you must figure how much reducing power or oxidizing power is left over (available) after the natural oxidizers and reducers in the ore have interacted and, to some extent, canceled out each other.

There are many reducers that can be used in fire assaying. Argols, also called wine lees, are widely used. Argol is a reddish crust or sediment that settles out of wine; it is used in the production of cream of targar. Wheat flour is the most popular reducer simply because it is so readily available.

Reducing Substances

Substance (One Part)	*Parts of Lead Reduced*
Charcoal	22 to 32
Coke	24
Wheat flour	15
Starch	11 to 13
Crude Argol	5½ to 8½
Hard Coal	25
Soft Coal	22
White Sugar	14½
Gum Arabic	11
Cream of Tartar	4½ to 6½

Establishing the Reducing Power of an Ore

In order to select an appropriate flux, you must first establish the reducing power (R.P.) of the ore. The R.P. of an ore is gauged by the amount of metallic lead 1 g of the ore produces (reduces) when fused with an excess of litharge. In a 10-g fire clay crucible, place a mixture of 3 g of the crushed ore whose R.P. you wish to establish, 10 g of sodium carbonate, 46 g of litharge (a clear excess of available litharge), 3 g of silica (barren quartz), and 1 g of sodium tetraborate. Place the crucible with the test charge in the assay furnace, close the door, and bring the furnace up to 1000°C. When the furnace reaches this temperature, turn the temperature back down to 900°C and hold this temperature for 20 min. After the 20 min at 900°C, raise the temperature back to 1000°C, and hold it at 1000°C for an additional 20 min.

The fusion is now poured into the cast-iron button mold. The slag is removed from the button and the button is weighed. The reducing power (R.P.) of the ore in question is the weight of the lead button divided by 3 g (the weight of the sample).

If, for example, the weight of the lead reduced from the litharge was 15 g,

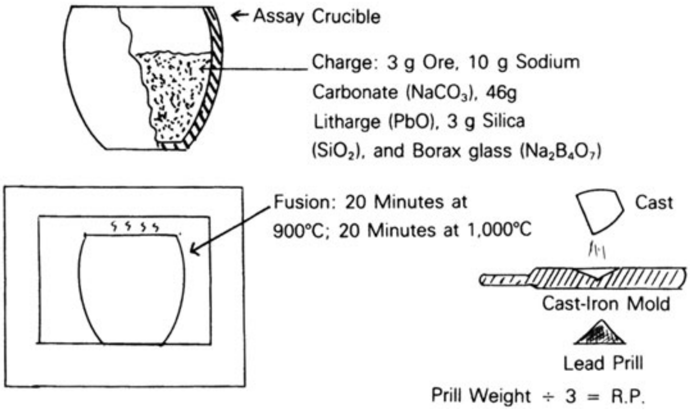


Figure 12.1. Establishing the reducing power of an ore

you would divide by 3 g and get 5, the R.P. of the ore. The ore is able to reduce 5 g of lead per gram of sample. See Figure 12.1.

The next step is to figure a charge that will produce a 28–30-g button from a sample of the 5 R.P. ore weighing ½ A.T. (assay ton)—14.58 g. Because precision in the ½ A.T. weight is not critical, you may round the 14.58 off to 15 g for your ore sample.

If you do nothing to counteract some of the ore's natural R.P., the sample will produce 5 g of reduced lead per gram of ore. This, multiplied by 15, means a 75-g button of lead from your ½ A.T. sample—45 g more than you want. You must include a sufficient amount of oxidizer to take care of the excess.

Looking under "Oxidizing Power" in the table of oxidizers, you will see that niter (saltpeter—KNO_3) has an oxidizing power (O.P.) of 4.2, meaning that 1 gram of niter will oxidize 4.2 g of lead. If you divide the excess of 45 g of reduced lead that the ore would naturally produce by 4.2, you will see that 10.7 g of niter must be incorporated in your charge to produce a lead button of the desired weight (30 g).

The accompanying table shows the composition of some typical charges. If you study these carefully, you will see that the differences in flux, reducers, or oxidizers among them is due to their different reducing and oxidizing powers.

Reducing and Oxidizing Powers of Common Minerals and Reagents

Reducers	*Reducing Power*
Arsenopyrite (FeAsS)	7
Carbon (C) (charcoal)	18 to 25
Chalcocite (Cu_2S)	5
Chalcopyrite ($CuFeS_2$)	8

Flour (wheat flour)	10 to 11
Galena (PbS)	3.4
Metallic Iron (Fe)	4 to 6
Pyrite (FeS_2)	11
Pyrrhotite (FeS)	9
Sphalerite (ZnS)	8
Stibnite (Sb_2S_3)	7

Oxidizers	*Oxidizing Power*
Hematite (Fe_2O_3)	1.3
Magnetite (Fe_3O_4)	0.9
Magnetite—Ilmenite	0.4 to 0.6
Niter (KNO_3) (saltpeter)	4.2
Pyrolusite (MnO_2)	2.4

Some Typical Charges

Ore: Iron pyrite (FeS_2) with a reducing power of from 10.56 to 11; Fe constitutes more than 10% of the sample.

Fusion Charge:

½ A.T. pyrite ore	30 g Na_2CO_3
60 g PbO	12 g SiO_2
10 g $Na_2B_4O_7$	0 g CaF_2
0 g flour	30 g KNO_3

Ore: Pyroxenite consisting of Si, Al, Fe, Mg, and Ca.

Fusion Charge:

½ A.T. pyroxenite	30 g Na_2CO_3
35 g PbO	4 g SiO_2
35 g $Na_2B_4O_7$	2 g CaF_2
3.2 g flour	0 g KNO_3

Ore: Pyrrhotite consisting of Si, Al, Fe, Mg, and Ni.

Fusion Charge:

½ A.T. pyrrhotite	35 g Na_2CO_3
70 g PbO	10 g SiO_2
10 g $Na_2B_4O_7$	0 g CaF_2
0 g flour	15 g KNO_3

Ore: Rhyolite consisting of Si and Al.

Fusion Charge:

½ A.T. rhyolite	25 g Na_2CO_3
50 g PbO	1 g SiO_2
5 g $Na_2B_4O_7$	1 g CaF_2
3 g flour	0 g KNO_3

Lead Assay

It is very important that you assay the litharge and any lead foil used in a crucible assay or scorification in order to determine the presence or absence of precious metal values in these materials. If the litharge or lead contains values, these values must be carefully weighed and deducted from the findings of any assay in which they are incorporated. Litharge and lead purchased for assay purposes as CP grade or assay grade carry an assay on the label; however, this assay label is sometimes incorrect, and it pays to check each batch yourself.

The following fluxes, with the addition of litharge in an appropriate quantity, can be used to assay for precious metal values. Flux #1: 4 parts by weight sodium bicarbonate, 4 parts potassium carbonate, 2 parts borax glass, and 1 part flour. Flux #2: 13 parts by weight sodium bicarbonate, 10 parts potassium carbonate, 5 parts borax glass, and 2½–4 parts flour. The usual amount of litharge added for the litharge assay is about 8 parts by weight to 1 part of either #1 or #2 flux.

The resulting button from the fusion is cupelled in the usual manner, and the bead, if any, is parted with nitric acid to get the silver and gold values. When you are assaying for extremely small values, the bead produced can be extremely small, making it difficult to weigh or even see. In such a case you should add to the assay sufficient pure (99.999%) gold or silver to increase substantially the size of the bead produced in the cupel. Of course, this portion is deducted when the values are weighed.

The lead foil you wish to assay is simply weighed and cupelled to a bead. As in the case of the litharge, you might have to add gold or silver to come up with a large enough bead. Flux #1 and flux #2 also can be used very effectively to assay lead ores. As you see by their makeup, if you add litharge to them, they will also make a good crucible flux and collector for assaying gold and silver ores.

Flux Combinations

The three general fluxes given in the following table are very similar to the two fluxes given for lead assays.

General Fluxes for Gold and Silver Ores

(Parts by Weight)

A.	Sodium Bicarbonate	5 parts	B.	Sodium Bicarbonate	1 part
	Potassium Carbonate	4 parts		Borax Glass	1 part
	Borax Glass	2 parts		Litharge	5 parts
	Flour	1 part		Ore	1 part
	Litharge	8 parts			

C.	Sodium Bicarbonate	3 parts
	Litharge	5 parts
	Borax Glass	2 parts

The basic lead ore or lead assay flux can be used as the starting place for making various fluxes for a wide variety of ores. You may think of this flux as our basic house flux.

House Flux:		
	Sodium Bicarbonate	8 g
	Potassium Carbonate	8 g
	Borax Glass	4 g
	Wheat Flour	2 g

Mix up a suitable supply of the above and store it in a large, dark, glass jar with a tight lid.

As I noted before, ores can be basic, acidic, or neutral in nature. A neutral ore is one that has no reducing power (R.P.) or oxidizing power (O.P.) such as a silicious oxide or carbonate ore containing no sulphides, arsenides, antimonides, or tellurides. A reducing ore is one that has a natural reducing power capable of reducing some of the litharge to metallic lead during fusion—ores that contain carbonaceous matter, sulphides, arsenides, antimonides, or tellurides. An oxidizing ore is one that exerts a natural oxidizing power on the litharge, thereby retarding or preventing reduction of the litharge to metallic lead. Oxidizing ores are those containing ferric oxide, manganese dioxide, or other oxidizing agents.

In order to flux the gangue to a slag that is thoroughly liquid, you need to follow one very basic rule: If the gangue is acidic in nature, you must use a basic flux; if the gangue is basic in nature, you must use an acidic flux.

Silica is acidic; nonetheless, it is easily fusible at assay furnace temperatures. Alumina is both acidic and basic and requires an acidic–basic flux mixture. Oxides of iron, manganese, calcium, magnesium, sodium, potassium, lead, zinc, and copper are basic in nature. Sodium oxide (Na_2O), potassium oxide (K_2O), and lead oxide (litharge) (PbO) are readily fusible at crucible assay temperatures, whereas the remaining oxides are not fusible at assay temperatures.

Given below are 14 recipes for flux makeup, using the house flux (H.F.), with additions, to obtain 28–30 g lead buttons from various ½ A.T. assay ore charges. After crucible fusion, the lead button in each case will contain the precious metal values of the ore in question.

#1. A neutral, oxidized, lead-free ore.

Ore (15 g) H.F. (30 g) Litharge (25 g)

Cover the charge with borax or salt; if you use salt in place of borax, add 3 or 4 g of borax to the salt cover.

#2. A neutral quartz ore.

Ore (15 g) Litharge (75 g) Argol (2 g)

Cover the charge with borax; if iron oxide is present, add some soda to the cover.

#3. A neutral quartz ore.

Ore (15 g) H.F. (30 g) Sodium bicarbonate (30 g) Litharge (20 g)

Cover the charge with salt (sodium chloride).

#4. A basic (oxidized), lead-free ore.

Ore (15 g) H.F. (30–40 g) Barren quartz or silica (15 g) Litharge (20 g)

Cover the charge with borax; if the gangue is an oxide or a carbonate add to the cover 2 or 3 g of argol.

#5. A basic (oxidized) ore containing barite ($BaSO_4$).

Ore (15 g) H.F. (40 g) Sodium bicarbonate (20 g) Litharge (25 g)
Barren quartz or silica (15 g) Iron nails (2)

Cover with borax.

#6. Galena ore concentrated to 85% lead values.

Ore concentrate (15 g) H.F. (20 g) Potassium ferrocyanide (10 g)

Cover the charge with salt and heat very slowly until the mass subsides; then bring to fusion temperature.

#7. Silicious galena ore.

Ore (15 g) H.F. (15 g) Sodium bicarbonate (20 g) Litharge (20 g)
Niter (5 g)

Cover the charge with salt. The amount of litharge will have to be adjusted up or down depending on the lead content of the ore.

#8. Neutral lead carbonate ore.

Ore (15 g) H.F. (30 g) Sodium bicarbonate (10 g) Litharge (15 g)

Cover the charge with borax; adjust the quantity of litharge up or down depending on the lead content of the ore.

#9. Iron pyrite ore.

Ore (15 g) Sodium bicarbonate (35 g) Litharge (20 g) Niter (5 g)
Barren quartz or silica (15 g) Iron nails (3)

Cover the charge with borax. Collect any matte that forms and scorify it with test lead or with the assay button. (Matte is a mixture of sulphides or iron and copper.)

#10. Concentrated copper pyrites ore.

Ore (15 g) Sodium bicarbonate (35 g) Litharge (30 g) Niter (5 g)
Barren quartz or silica (15 g) Iron nails (3)

Cover the charge with borax. Scorify any matte that forms with lead. (The purpose of nails in an assay is to convert sulphides into iron sulphides.)

#11. Silicious tellurides.

Ore (15 g) H.F. (30 g) Sodium bicarbonate (30 g) Litharge (40–80 g)

Cover the charge with salt. If the button is hard or brittle, scorify it with lead. With silicious tellurides, a scorification assay is usually preferred to a crucible assay.

#12. Silicious tellurides.

Ore (15 g) Litharge (80 g) Argol (2 g)

Cover the charge with salt.

#13. Arsenical ore.

Ore (15 g) Sodium bicarbonate (15 g) Litharge (30 g)
Potassium ferrocyanide (17 g)

Cover the charge with salt. Most arsenical ores are assayed by scorification.

#14. Slags from all operations.

Slag (19.116 g) (serves as 1 A.T.) H.F. (30 g)
Sodium bicarbonate (40 g) Litharge (10 g) Borax glass (10 g)

Cover the charge with salt. If the slag contains matte, add 1 iron nail.

Slags

The color of a slag, like the color of the bead in a borax bead test, can tell you a great deal about the material being assayed. You should always examine your slags very closely. In a scorification assay, the color of the thin coating of slag left on the surface of the scorifier is a good clue to the approximate composition and amount of the metal present in the material that has been scorified. See Figure 12.2.

Scorifier Slags

A light to dark green slag indicates a small to large amount of copper. If much iron is in the ore, it can mask the green with black. However, if the copper is masked, a rescorification will show the green. This green color comes from a combination of the blue produced by cupric silicate and the yellow produced by lead silicate.

A slag that is deep red through various shades of brown to yellow-brown contains large amounts of iron.

A lemon yellow to light yellow slag indicates lead (and the absence of other metallics).

A beautiful cobalt blue slag indicates cobalt.

A brown to black slag could indicate nickel or a combination of other metals. The presence of nickel is confirmed when the button is cupelled: The cupel will be covered with a thick film of green nickel oxide if much nickel was present in the button.

A wine-colored slag indicates the presence of manganese. Slags of other colors can be identified by referring to the colors obtained in bead tests.

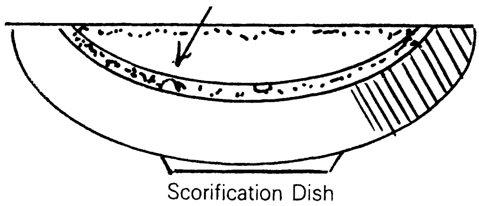


Figure 12.2. Slag color as an indicator

Crucible Assay Slags

The colors of a crucible slag tells a different story, due to the difference of the slag composition. Crucible assays contain larger amounts of borax and silica than scorification assays do, along with smaller amounts of litharge.

Green slags indicate ferrous silicates, not copper.

Brick red slags indicate copper and the absence of iron. The color comes from either cuprous silicate or cuprous borate.

White to gray white (opaque) slags indicate calcium, magnesium, aluminum, or zinc.

Cobalt blue slags indicate cobalt.

Purple to light pink slags usually indicate manganese.

Regardless of color indications, slags must be examined for shot metal, and they should be assayed for value.

Aside from being composed of the proper elements in the correct proportions for a particular ore, a good flux must have the following characteristics:

1. It must have a formation temperature within the temperature range of the assay furnace.
2. It must remain sufficiently thick at or near its formation temperature to allow any precious metals present to be released from their chemical or mechanical bonds with the gangue before the flux allows the collector particles of lead to drop down and alloy with the precious metal values.
3. It should become sufficiently thin when heated above its formation temperature to allow the reduced lead globules to settle through it easily.
4. It should completely decompose the gangue to a fluid slag, and it should have a very low affinity for gold and silver.
5. Its chemical composition should be such that it does not excessively attack or flux away the crucible.
6. Its specific gravity should be low enough to give a good separation between the lead and the slag.
7. When the slag is cold, it should be homogeneous and easily removed from the button.
8. It should not retain higher oxides (oxides containing more than two O atoms per molecule) of metal, and yet, at the same time, should contain all the impurities present in the gangue.
9. It should be free of sulphides (unless you are using nails in the assay).

When you have worked up the desired flux—based on your preliminary fusion to determine the reducing power of the ore and on your examination of the ore—

and have carefully assayed your reagents, you can proceed with your fusion. See Figure 12.3.

Cupellation

Cupellation consists of oxidizing the lead fusion (containing the values) back into litharge (PbO), at which point the cupel will absorb any base metal oxides, leaving the precious metal values in the cupel.

The cupel is a shallow cup made of compressed bone ash with or without a binder added. A high-grade bone ash cupel will absorb its weight in litharge. The cupel should weigh approximately one-third more than the weight of the lead button being cupeled. See Figure 12.4.

You can make your own cupels or purchase them. There are several substitutes for bone ash—such as cement and magnesia. However, these are not really satisfactory, and bone ash cupels are both effective and inexpensive.

The end product of cupellation is a small doré bullion bead composed of the less readily oxidized metals—generally, silver and gold, but also any metals of the platinum family that were present in the fusion.

The cupellation procedure is simple: If you follow it step by step, you should get good results with few problems. If you are careless, though, you can lose in excess of 5% of your silver value during cupellation. Cupellation must be done methodically.

Step 1: Heat the cupellation furnace (assay furnace) to 850°C.

Step 2: Set out some cupels that are sound, dry, and free from dust. Purchased cupels are usually the proper density and are sound. The cupel has to be sufficiently permeable to allow the litharge to be easily absorbed, but at the same time not be so porous as to allow the bead or lead to sink in. The surface tension of the lead and of the resulting doré bead is such that neither will penetrate into the cupel. Place the cupels in the furnace with an extra row of empty cupels between them and the door. See Figure 12.5.

The reason for this row is to prevent the cupels in use from cracking due to the thermal shock to which they would be subjected when the door of the furnace is opened. If a cupel cracks when in use, it is lost. Heat the cupels for 15–20 min with the door closed and the temperature at 850°C.

Step 3: Hammer the lead fusions into rough cubes ("prills"). Open the door, quickly place the prills in the hot cupels, and reclose the door. See Figure 12.6. Use the peep hole in the door to occasionally observe what is occurring inside.

Each lead cube quickly melts and spreads out. The top of the lead pool in the cupel is covered with a black layer of lead oxide, slag, dirt, and other solids that have floated to the top. See Figure 12.7. In a minute or two, this covering layer flows to the edge of the cupel and starts to soak into the cupel. The metallic lead, which had been covered, is then exposed. This is called "opening up" or "uncovering." See Figure 12.8.

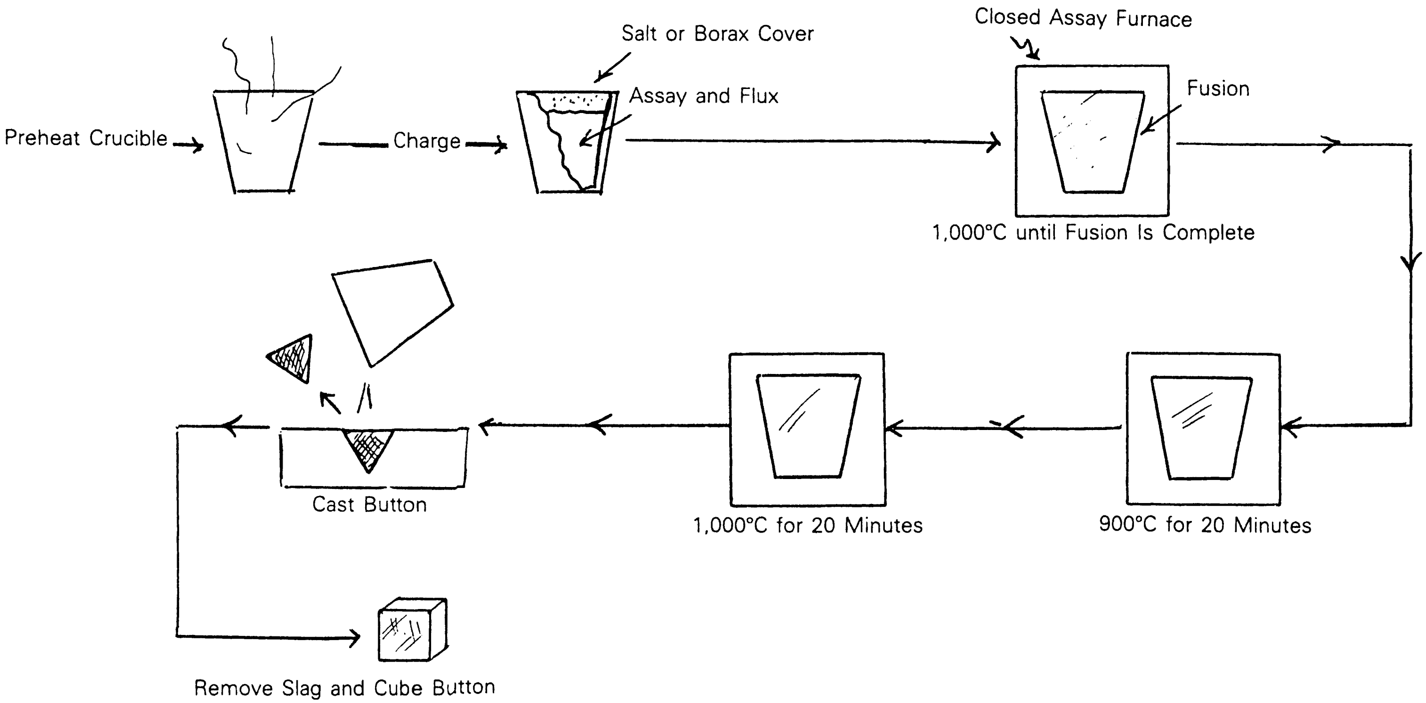


Figure 12.3. Flowchart for crucible fusion

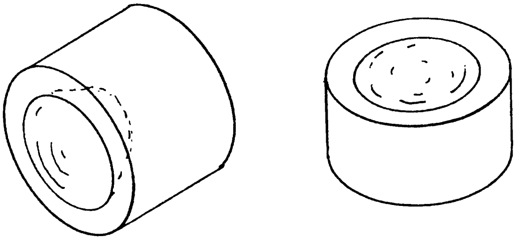


Figure 12.4. Bone ash cupel

At the opening-up stage, the remaining solids are swept aside and the exposed bare surface of the lead begins to burn. The lead oxide continues to drain off and soak into the cupal, although a small percentage of the lead vaporizes. These lead fumes should be avoided at all costs. See Figure 12.9.

Lead can be an extremely dangerous substance. It is cumulative, building up in your body tissues and bones, and lasting for years. One milligram of lead for every 10cc of air is toxic. Daily absorption of only 1 mg eventually results in a lethal amount in your system.

A total of 2.5 g of lead adsorbed in your bones and system is more than enough to cripple or kill you. The lead vapors (lead smoke) from the assay furnace, if breathed, go directly from your lungs into your bloodstream in a matter of

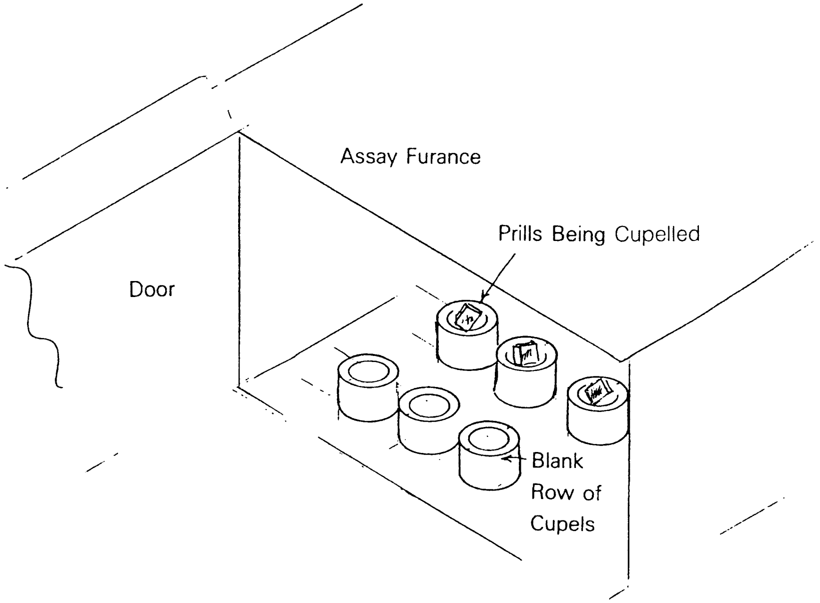


Figure 12.5. Cupel setup in assay furnace

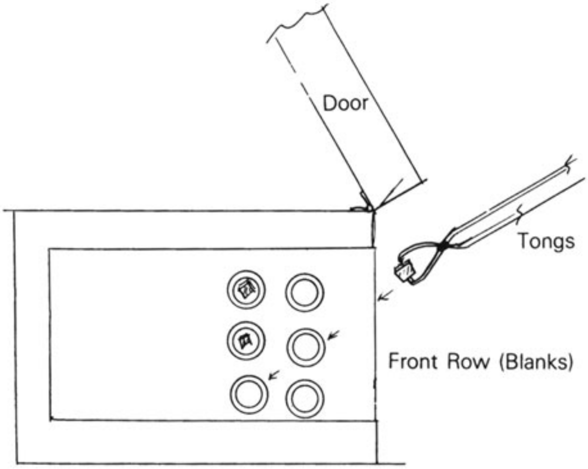


Figure 12.6. Loading prills into cupels

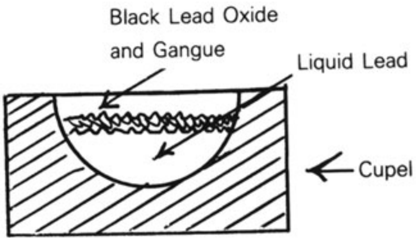


Figure 12.7. First action in cupel

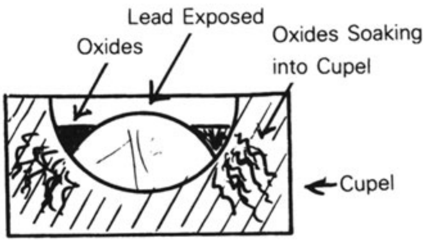


Figure 12.8. Cupel "opening up"

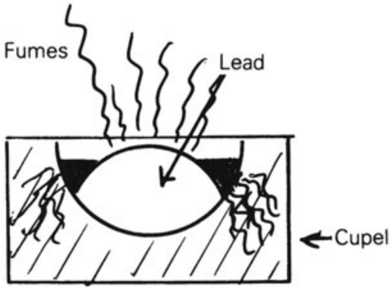


Figure 12.9. Burning the lead to form litharge

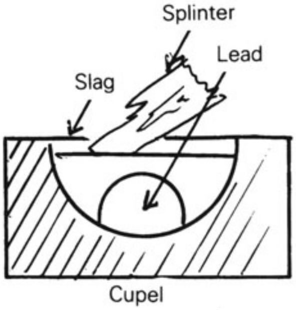


Figure 12.10. "Opening" the cupel using a splinter of wood

seconds. You can pick up lead fumes while working with the blow pipe, soldering with lead solder, handling used cupels (which can contaminate your hands and clothes), or breathing dust from lead ores or other lead sources.

The symptoms of lead poisoning vary from person to person but may include dizziness, slurring of speech, and a blue line above the teeth on the gums. Once in the bloodstream, lead gets pumped all through the body, so it can end up affecting all the body's organs. Lead poisoning has sent so many assayers to the big assay shop in the sky that, in the trade, lead poisoning is referred to as Assayer's Disease. Painters handling lead-based paint used to fall victim to lead poisoning also.

There are a number of safety measures that you should observe to minimize the risk of lead poisoning. Wear a respirator or have good draft, wear gloves, keep the work area free from dust, and do not under any circumstances handle used cupels or scorification dishes with your bare hands.

A cupel that fails to "open" is called a "frozen cupel"; it usually results from a cupel's having too thick a layer of material over the lead to get rid of it all, or from a cupel's being too cool. If you open the door (avoiding contact with fumes), place a small splinter of dry wood on the unopened cupel, and then close the door, the wood will do two things: It will burn, raising the temperature of the cupel; and when the wood is reduced to carbon, the carbon—being reducing in nature—it will usually reduce some of the lead oxide to metallic lead, thus opening the cupel. See Figure 12.10.

If you have several cupels that fail to open, you can lay a stick of dry wood in front of them on the hearth, and this will usually open them. See Figure 12.11. During the entire operation, keep the door closed until all the cupels have opened; open the peephole only for an occasional quick look, then close it promptly. From time to time, a cupel will not open regardless of what you do; it is simply part of the game.

Step 4: When the cupels have all opened and the lead is being oxidized and absorbed by the bone ash, the oxidizing of the lead is exothermic, and the cupel is acting as an insulator. This significantly raises the temperature of the lead

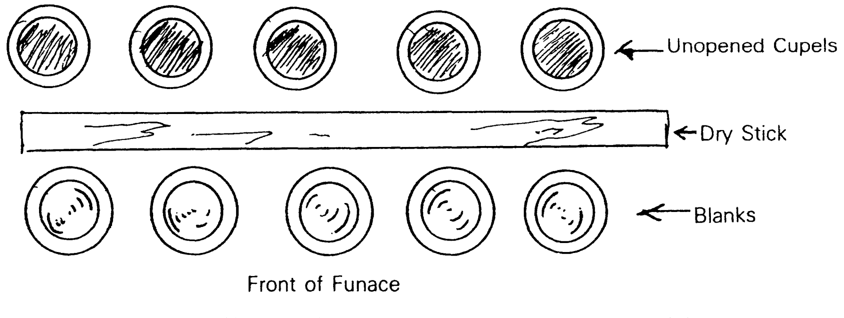


Figure 12.11. "Opening" a row of cupels using a stick

being oxidized, and unless the temperature of the furnace is lowered from 850°C, you will promote the loss of silver. In such a case, the lead becomes considerably brighter than the furnace walls. This is called "driving the cupel" and is a poor practice.

Once the cupels have opened, the furnace temperature must be lowered to a point at which the forming litharge is maintained slightly above its melting temperature. At this point, the burning lead is red instead of yellow or dazzling yellow–white. As long as the lead and litharge are kept at a temperature at which the lead continues to burn and at which the forming litharge remains molten long enough to soak into the bone ash cupel, you will get the results you want.

If some of the litharge that vaporizes condenses as dendritic crystals on the cupel above the burning lead, it is a very good sign that any silver loss will be extremely minor. These dendritic crystals are called "feathers." See Figure 12.12.

Step 5: Near the end point, when the lead is nearly gone and only a thin coating is left on the doré bead, raise the temperature of the furnace to keep the molten alloy of silver, gold, and other values in a liquid state and to drive off the last bit of lead remaining.

When you get down close to the end point, there is a play of colors in the cupel, and the bead appears to spin about the cupel wildly. At the very end, the bead may become very bright for a split second; this action is called the "blick" or "wink." The cause of this is that the liquid metal (doré bead) supercools at the instant the last of the lead leaves it, and, when it goes from a liquid to a solid, the latent heat raises the temperature to produce the "wink" or "blick."

If the doré bead is quite large and contains much silver, the cupel should be moved toward the front of the furnace and covered with a hot cupel so that the top surface will remain liquid (not crust over) as the bead solidifies. Silver, when molten, will absorb any oxygen released at the moment of solidification—the familiar "spit." In cupellation, if a solid crust forms around a liquid core, as the core then solidifies, the "spit" of released oxygen remains trapped by the crust and builds up pressure until a miniature explosion occurs. The explosion fragments the crust (an occurrence known as "sprouting"), resulting in physical loss of some of the value. See Figure 13.13.

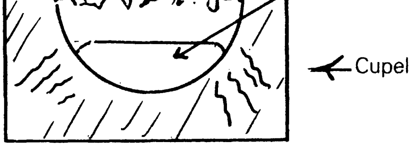


Figure 12.12. A feathered cupel

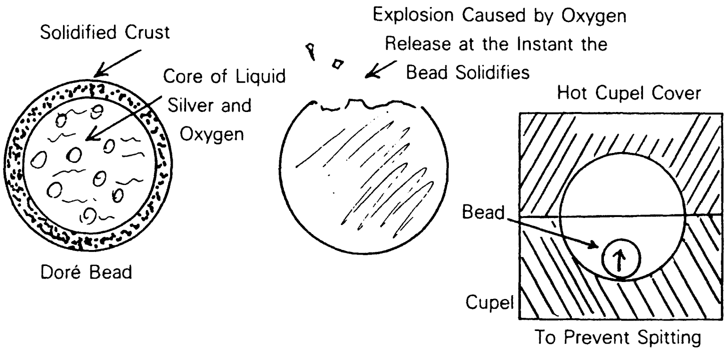


Figure 12.13. Doré bead "splitting"

Step 6: Carefully clean and weigh the bead recovered from cupellation. You are now ready to part the silver with nitric acid.

When gold is alloyed with less than three times its weight in silver, you will find it difficult to accomplish a good clean parting because the gold protects the silver from attack by the nitric acid. When faced with such a bead, you simply have to add enough 99.9% pure silver to make the silver in the sample weigh over three times as much as the gold. Wrap the sample in pure lead foil and recupel this to get a doré bead that will part properly.

To avoid this process of inquartation and double cupellation, consider adding the pure silver at the stage of crucible fusion or first cupellation. You want to produce a doré bead that is at least three-quarters silver and at most one-quarter gold. The word inquartation means one quarter. Of course, you must deduct the weight of added silver or gold from your assay totals.

Mix one part nitric acid with seven parts distilled water, place this in a small beaker or porcelain dish, and bring it up to almost boiling; then drop the doré bead into the acid solution. The acid should start immediately to dissolve (part) the silver from the doré bead.

If the bead fails to start parting, add full-strength nitric acid, drop by drop, until the bead starts to react with the acid solution. The nitric acid used for parting must be CP reagent grade. If the nitric acid contained any chlorine, it would in reality be a mild aqua regia, putting some of the gold from the doré bead into solution and coating the bead with a precipitate of insoluble silver chloride. If other halogens—such as bromine or iodine—were present in the nitric acid, they would cause the metals to behave similarly.

If in doubt, test the acid. Place a few cubic centimeters of acid in a clean test tube, tip the tube, and drop a few drops of silver nitrate solution so that they run down the side of the test tube and come into contact with the acid without mixing with it. If a ring of precipitate forms at the interface of the acid and silver nitrate, the acid is contaminated with a halogen impurity. See Figure 12.14.

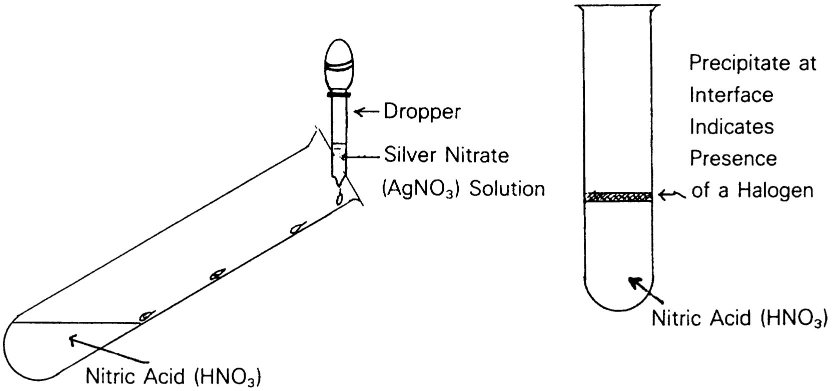


Figure 12.14. Checking for halogen impurity in nitric acid

To check for chlorates, place a few cubic centimeters of the acid in a small beaker, add a little silver nitrate solution, and then add a few small pieces of copper, zinc, or silver to decompose the chlorates. If the acid being tested is contaminated with chlorates, the familiar white, curdy silver chloride will be precipitated.

Unless the acid solution is hot when you drop the doré bead into it to part it, the gold will not stay together as a coherent, black sponge of gold. If the gold sponge is allowed to disintegrate into small particles, it becomes a problem. Therefore, you should keep the acid solution hot during the entire parting operation.

If the bead to be parted weighs more than a few milligrams, it should be flattened on a polished anvil with a polished hammer and rolled or flattened to about ten-thousandths of an inch thick. A very large bead might have to be annealed several times to avoid being split or cracked during flattening. This is accomplished by heating the bead (while holding it in platinum tweezers) to a red heat and dropping it into cold water between flattenings on the anvil or rolls. The metal is then rolled into a spiral or cornet for parting.

Small porcelain-glazed evaporation dishes are great for parting. Being white, they allow any small black gold particles that happen to come loose from the sponge to be easily seen, making it easier to retain them when decanting the acid solution and when washing the sponge.

The final washing of the sponge is tricky; it should be done by directing the wash water from the wash bottle tangentially against the inside rim of the evaporating dish. You do not wish to hit the sponge directly with the wash water stream because that might dislodge gold particles from it. You want to swirl the sponge around gently. This washing should be done a minimum of three times (preferably five times). Decant each wash into a glazed casserole dish so that if any bits of gold were washed or decanted from the sponge, you can clearly see these specks in the casserole dish and can recover them.

The sponge should be washed with distilled water. The sponge is then annealed by heating to a red heat (do not quench), at which point it will assume its correct, gold color. If you failed to wash the sponge properly or did not part off all the silver, the sponge after annealing will be off-color—lighter than pure gold. You will then be faced with inquarting, parting, and recupelling. Each time you have to repeat a process, due to an error on your part, you increase the chance of error in the final results. Take your time. See Figure 12.15.

I believe that metals of the platinum group—platinum, iridium, osmium, palladium, rhodium, and ruthenium—should not be handled by fire assaying, but by wet chemical means. Nonetheless, you will pick up platinum metals during fire assaying of various ores, black sands, mattes, speisses, base bullions, sweeps, slimes, and electronic scrap.

Small amounts of platinum—as little as 1.06%—in a cupel bead will give the bead a frosted appearance, as (to a lesser degree) will palladium. A minor quantity of tellurium will also give you a frosty looking bead. It is easy to be fooled, and it takes some years of experience to recognize and distinguish the various indicators.

At the initial examination of the ore, under the microscope or under a magnifying glass in a gold pan, you will usually—but not always—become aware of the platinum-group metals that are present.

A good procedure to follow, if you suspect the presence of any or all of the platinum group, is to divide a raw sample of the material to be tested into two equal batches. Run a standard assay on batch #1, and weigh the cupel bead (but do not part the bead, as palladium is soluble in hot nitric acid). Look for a frosty appearance. Now take batch #2 and run a fire assay exactly as you did on batch #1, with one exception: add 3 mg of 99.9% pure gold, in the form of 0.005-in. diameter wire, to the crucible fusion. The pure gold you add will pick up (collect) the platinum-group values. Weigh the beads from the two assays, remembering to subtract the 3 mg of gold you added to the second batch. If the second assay

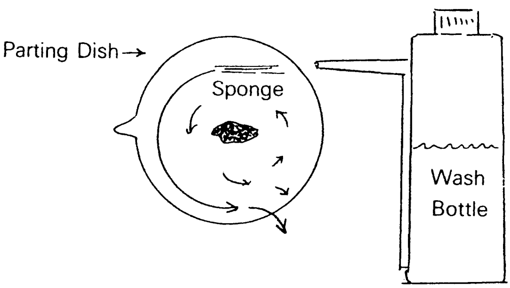


Figure 12.15. Correct method of washing the sponge

bead (less the 3 mg of added gold) weighs more than the first assay bead, the difference is attributable to the presence of platinum-group metals.

For example, if bead #1 weighs 6 mg and bead #2 weighs 12 mg, you first subtract the 3 mg of gold you added to batch #2, then subtract 6 (the weight of bead #1) from 9 (the adjusted weight of bead #2). The remainder of 3 mg represents the total weight of platinum-group metals in each assay sample.

Whenever you find flakes or nodules of gray or grayish material that are not fusible under the blow pipe and are insoluble in single-acid solutions, you may be fairly sure that the material belongs to the platinum group of metals.

The Glow Test

The glow test has been around for many years, but it is still a valid and reliable test. It is based on the catalytic action of finely divided particles of platinum-group metals on the oxidation of hydrogen in illuminating gas.

The test is quite simple. Digest a few pinches of the sample in hot aqua regia and treat it as you would a wet extraction—evaporating the solution to a syrup-like consistency several times, with additions of hydrochloric acid between evaporations, to expel all the nitric acid. Next, dip a thin bit of asbestos paper in the solution and then heat it with a soft flame. This will drive off the aqua regia and dry the residue. The residue consists of finely-divided platinum metals, reduced from the chorides of these metals.

If you now hold the treated paper over an unlit jet of gas, the powder will begin to glow and the gas jet will light; or you can, after the soft drying, heat the paper to a red heat, turn off the gas, let the paper cool to a point below visible red, and turn the gas jet back on: The paper will glow at once if any platinum metals are present. See Figure 12.16. Platinum and palladium have the ability to soak up gases. In doing so, they become quite hot, and this is what produces the glowing effect.

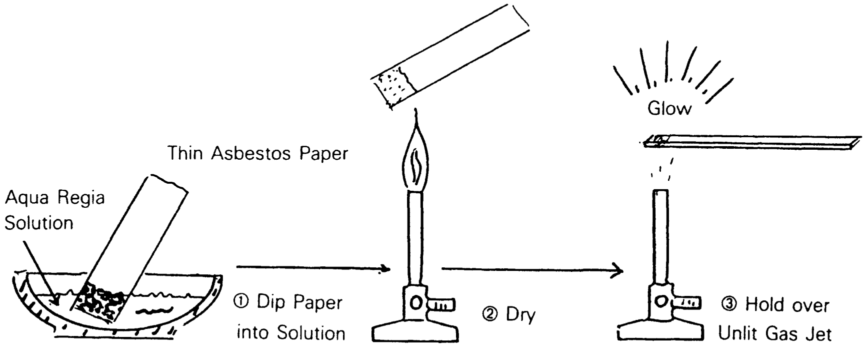


Figure 12.16. Glow test for platinum

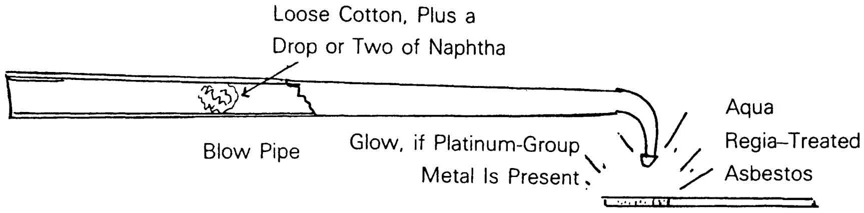


Figure 12.17. Glow test using the blow pipe

The glow test is quite sensitive and will indicate the presence of as little as 0.005 mg of palladium, 0.0009 mg of rhodium, 0.002 mg of platinum, or 0.005 mg of iridium. It will not show osmium or ruthenium, but these two metals are the least important in the group.

During the Depression, there was a popular cigarette lighter on the market whose starter mechanism was based on the glow reaction of fine platinum and palladium particles with naphtha fumes.

The treated sheet of asbestos can also be checked for the presence of platinum metal values by placing a small ball of cotton in the blow pipe, dropping a few drops of naphtha on the cotton, and blowing the naphtha fumes onto the treated asbestos. See Figure 12.17.

Summary and General Rules

When a material under investigation (ore, slimes, or sweeps) is mixed with the correct amounts of flux formula, litharge, and reducing agent—such as flour, argol, or a sulphide—and is heated strongly (fused) in a crucible, the litharge will reduce to metallic lead. These droplets of reduced lead descend through the fused material (charge) by gravity; in doing so, they collect the metallic values. This movement of reduced lead through the charge is called "lead fall."

The result of the lead fall is the accumulation of a blob of liquid lead at the bottom of the crucible, in which all the metallic values that were present in the charge are contained. This lead blob is cast into a conical button and mechanically separated from the slag (unwanted gangue) of the fusion.

The lead button from the fusion should be soft and malleable, being composed of lead, gold, and silver. If the button is hard and brittle, other metals are present, requiring wet chemical treatment or other special treatment for separation. If matte is present, which is undesirable, it will appear as a gray, brittle, sulphide button on top of the lead button. If speiss is present, which is also undesirable, it will be in the form of a hard arsenide button on top of the lead button. Speiss consists of an arsenic or antimony compound of iron, often with nickel, copper, or other metals present.

Sodium chloride, used as a cover on the fusion charge, or sodium sulphate, formed during fusion, will be on top of the slag when the fusion is poured.

In order to select the proper flux for a particular ore, examination and testing are necessary to determine if the ore is neutral, acid, or basic, and reducing or clayey.

For silicious ores, you need a bisilicate slag in order to produce a 28–30 g lead button. Use soda ash equal to the weight of the assay. Use litharge equal to 1½ times the weight of the assay, plus 30 g for the button. Use borax equal to 6% of the weight of the assay. Use 2½ g of flour as a reducer for the 30 g of litharge you allowed for the lead button. These proportions will work if the assay has zero reducing power (make an R.P. test).

Basic ores are treated in the same manner as silicious ores with these exceptions: add barren quartz or silica equal to the weight of the assay; add borax glass equal to 85% of the weight of the added quartz or silica; if the assay contains iron oxide or manganese oxide, use more than 2½ g of flour.

Clayey ores require easily fused fluxes; the addition of cryolite or some other fluoride will help to accomplish this.

For an ore that has a significant reducing power, you must use less or no reducer (usually this means using less flour), and you must use potassium nitrate (saltpeter) as an oxidizer to limit the lead fall to 28 or 30 g. Use iron nails as a reducing and desulphurizing agent.

General Rules on Cupellation

Cupels should be composed of bone ash, Portland cement, or magnesia. Heat them thoroughly before putting the lead into them. If, after insertion of lead and heating, a cupel fails to open, add a wood splinter.

Do not drive the cupel after it has opened; instead, reduce the furnace temperature and crack the door to provide air to assist in the lead oxidation. When the lead has almost completely reconverted to litharge and soaked into the cupel, raise the furnace temperature to complete the lead removal (drive it).

When the bead flashes upon solidification (the blick), you have reached the end point.

General Rules on Parting the Bead

Weigh the bead; then flatten or roll it.

The parting acid must be free of chlorides—use chemically pure nitric acid. The usual mixture is one volume of CP nitric acid and seven volumes of distilled water, heated so that it is hot but not boiling in the parting cup.

After the silver has gone into solution, decant the acid off and wash the gold sponge several times with warm distilled water, using a swirling action. Dry the sponge, heat it to a red heat to anneal it, and weigh. The sponge weight subtracted from the bead weight leaves a remainder equal to the silver weight.

Remember, if the bead is too rich in gold, a good, complete parting is hard to get. In such a case, you will have to add silver (inquartation); to avoid recupellation of the new bead, try to catch this gold imbalance at the fusion stage and add fine silver at that point. A true inquartation produces a combination that is three parts silver and one part gold. However, the best results will be obtained if you produce a bead that is 8 or 10 parts silver to 1 part gold.

Be especially careful not to lose any of the little pieces of black gold that might become disengaged from the sponge during parting or washing.

Scorification

Scorification is a quick, simple type of fire assay in which you use CP test lead in place of litharge to perform an oxidizing fusion of the sample material with lead and borax in a shallow, open, fire-clay dish (scorifier). See Figure 12.18. Scorifiers run from 2 to 3 in. in diameter. The most common sizes used are 2¼, 2¾, or 3 in. in diameter.

The weight of the ore to be assayed will range from 0.05 A.T. to 0.25 A.T., the weight of the test lead used is from 30 to 70 g, and the weight of the flux borax glass is from 1 to 5 g.

Typical Scorifier Charges

Ore: Galena (0.10 A.T.) Test lead: 15–18 g Borax glass: 0.5 g
Ore: Galena with zinc blende and pyrites (0.10 A.T.) Test lead: 20–35 g Borax glass: 0.4–0.8
Ore: Iron pyrite (0.10 A.T.) Test lead: 30–45 g Borax glass: 0.3–0.8 g
Ore: Arsenical pyrite (0.10 A.T.) Test lead: 45–50 g Borax glass: 0.3–1.5 g Litharge: a pinch
Scorify at high temperature.
Ore: Gray copper (0.10 A.T.) Test lead: 35–48 g Borax glass: 0.3–0.5 g
Scorify at low temperature.
Ore: Zinc blende (0.10 A.T.) Test lead: 30–45 g Borax glass: 0.3–0.6 g Iron oxide: a pinch
Scorify at high temperature.
Ore: Copper ores and mattes (0.10 A.T.) Test lead: 35–40 g Borax glass: 0.3–0.5 g

Figure 12.18. Scorification dish

Scorify at low temperature and rescorify the bullion with lead. Cupel the resulting button.

Ore: Tellurides (0.10 A.T.) Test lead: 50 g Borax glass: 0.3 g

Cover the charge with a thin layer of litharge. Scorify and then rescorify. Cupel this rescorified button.

Ore: Various silicious ores (0.10 A.T.) Test lead: 25–30 g Borax glass: none

Ore: Various basic ores (0.10 A.T.) Test lead: 25–30 g Borax glass: 0.5–2.0 g

If the ore is high in lime, magnesia or a pinch or two of sodium carbonate will assist.

Ore: Basic ores containing some barium sulphate

Proceed as above for basic ores, but use slightly less borax glass

Ore: Lead carbonate (0.10 A.T.) Test lead: 10–15 g Borax glass: 0.5 g (maximum)

The Scorification Procedure

The scorification assay is by no means limited to ores alone; it is extremely useful in assaying finely divided metallics, precipitates, slimes, or sweepings.

Assume that you want to assay a sample of silver-bearing ore. The scorification assay will amount to a reverse Parks process plus a cupellation proposition. Usually scorification assays are done in multiples—three to five scorifications done on the same sample material. In this example, plan for three. Grind the sample until it is very fine and mix it thoroughly. Weigh out three portions of test lead, weighing 40 g, 50 g, and 60 g, respectively. See Figure 12.19.

Set out three dry, clean scorifier dishes, with diameters of 2½ in., 2¾ in., and 3 in., respectively. Place 20 g of test lead in the 2½-in. dish, 25 g of test lead

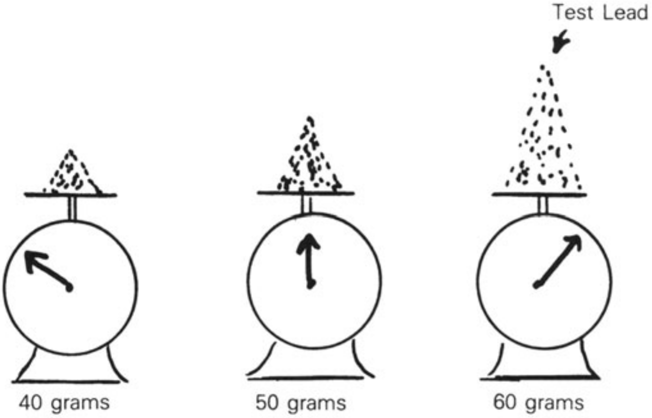


Figure 12.19. Scorification assay, first step: weighing test lead

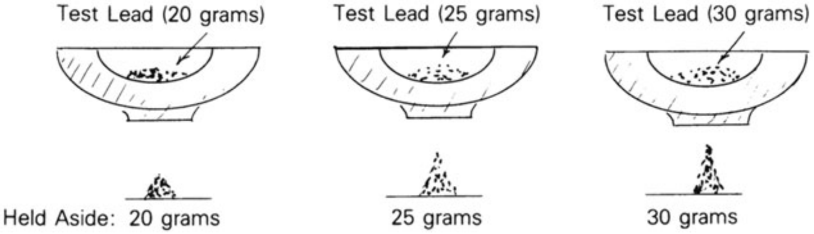


Figure 12.20. Scorification assay, second step: splitting the portions of test lead

in the 2¾-in. dish, and 30 g of test lead in the 3-in. dish; hold aside the remaining 20, 25, and 30 g of test lead from the three original portions. See Figure 12.20.

Now weigh and separate three portions of the finely ground, well-mixed assay, of exactly 0.1 A.T. (2.9166 g) each. Place each of the 0.1 A.T. assays on top of the test lead in each scorifier, mix the contents of each well with a thin, stainless steel spatula, and cover each mixture with the remaining 20, 25, and 30 g of test lead from the original portions. See Figure 12.21.

At this point, you have 20 g of test lead mixed with 0.1 A.T. of assay and covered with another 20 g of test lead in the 2½-in. dish, 25 g of test lead mixed with 0.1 A.T. of assay and covered with another 25 g of test lead in the 2¾-in. dish, and 30 g of test lead mixed with 0.1 A.T. of assay and covered with another 30 g of test lead in the 3-in. dish. You are now ready to do the scorification.

Heat the assay furnace to a yellow to light red heat; then place the scorifiers about midway in the furnace and close the door. Allow the contents of the scorifiers to become completely fused. This part of the operation is called the fusion stage or fusion period.

When everything is well fused, open the door to let in fresh air. This will supply the oxygen to oxidize the lead and to oxidize any sulphides and base metals that may also be present. The precious values (gold and silver) will be taken up by the lead. The patches of one gangue floating on the lead will progressively become smaller and smaller until they finally disappear, leaving what is called the "eye"—a bath of molten lead surrounded by a ring of slag. See Figure 12.22. This stage is called the roast.

The vapor rising from the roast and its odor often indicate the nature of the

Figure 12.21. Scorification assay, third step: combining ore and lead and covering with lead

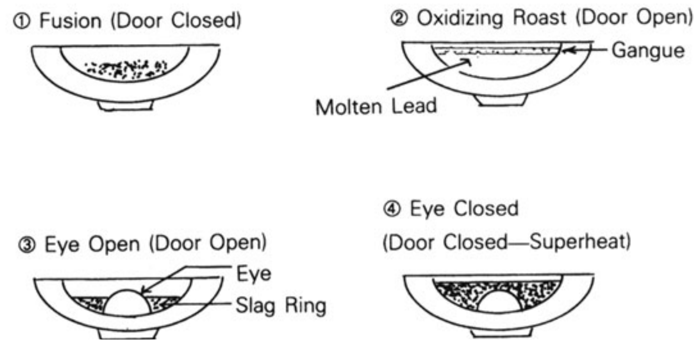


Figure 12.22. Scorification assay, fourth step: fusing mixture through "closing the eye"

ore. You may recall a similar situation in your blow pipe examinations on the charcoal or plaster tablets: sulphur, with its rotten egg odor and clear gray fumes; arsenic, with its grayish white fumes; zinc, with its burning and snow-zinc oxide; and antimony, with its reddish fumes, all are readily identifiable.

If you examine known ores and compounds as a familiarization study, you can become very good at identifying exactly the elements present and the reactions occurring during a scorification.

At the "eye" stage of the roasting period, the eye is open and surrounded by liquid slag, with no visible solid gangue floating on the eye or in the slag circle around the eye. The precious metals, if any were present in the sample, are now incorporated in the lead eye. See Figure 12.23.

The next stage, the actual scorification, is also known as "closing the eye." Without any change in heat, you simply allow the lead in the eye to continue to oxidize (into litharge). As the eye oxidizes, the amount of slag is increased, raising its level until finally the slag covers ("closes") the eye. See Figure 12.24.

Once the eye is closed, the scorification is complete. At this point, because you do not wish to continue the oxidation, you close the furnace—to exclude

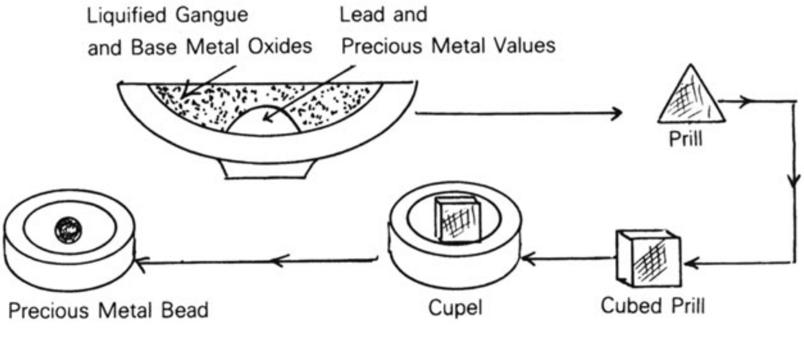


Figure 12.23. Scorification assay end point

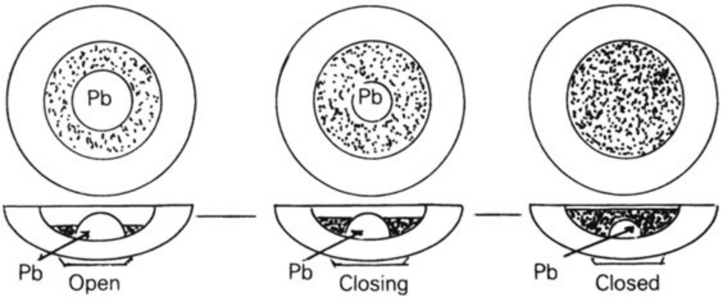


Figure 12.24. The "eye" closes

new oxygen—and raise the temperature for a few minutes. This will ensure that the slag is in a thoroughly molten state. You then pour the button into the button mold. Remove the slag, hammer the button into a cube, and cupel it in exactly the manner you would a button from a crucible fusion.

As in the case of a crucible fusion and cupellation, you may have to rescorify the bead under certain circumstances.

Remember to assay your test lead in order to establish exactly how much silver and gold it is carrying, as a benchmark. You can perform this as a crucible assay or a scorification.

If you choose the scorification method, scorify about 120 g of your test lead in a 4-in. scorification dish, reduce it until the eye closes and you have a 15–20-g button. Cupel, weigh, and part the bead with nitric acid. If the lead button is too large, rescorify it until it is small enough. If the resulting precious metal bead is too small to measure accurately, you will have to resort to inquartation with silver, followed by rescorification and cupellation.

If you have to make an inquartation for any reason, as part of any type of refining or assaying, you must have an accurate assay of the material you are using for the inquartation. If you do not, you will be adding an uncertain quantity of value to the assay, which will throw off your calculations.

You can purchase silver and gold to use for inquartations from your supplier. Each piece of this material is carefully weighed by the supplier and carries a notation of its weight and assay. These pieces of metal purchased for inquartation are called "aliquots," which is derived from a Latin mathematical term meaning an even partitioner or divisor; 3 is an aliquot part of 6, but 5 is not. The metal pieces are also sometimes called "parties," from a French word meaning "part" or "portion." Of course, if you do not purchase assayed and weighed aliquots for your inquartations, you must assay the material yourself.

Test lead in the form of granules or foil can carry an assay, but more than once I have found using this to be imprecise enough to throw off the assay in which I was using it. The best practice is to assay all your reagents, solid or liquid, and mark any corrections that need to be made.

13

Thin-Layer Chromatography

The separation of a mixture of compounds in a solution via thin-layer chromatography, often called paper chromatography, is a relatively simple and inexpensive method of analysis which requires a minimum amount of inexpensive equipment and reagents. One wonders why you see very little thin-layer chromatography being done to separate mixed bags of precious metals in solution, especially in small operations.

With the classic fire assay, you wind up with a precious metal bead by cupellation. You weigh the bead to ascertain the ounces per ton, parts per million, and so forth. However, this information is quite limited. After you part off the silverwith HNO_3, you are still in the dark.

Some will say that they can come up with a good guess visually [that is, the bead is 10% PMG (platinum metal group) and 90% Au, etc.]. This is not so. You are faced with taking the bead through one of the many methods of separation to come up with the answer. Wet chemical gravimetric, liquid/liquid separation, potentiometric titration, spectrophotometer, x-ray fluorescence, atomic absorption (AA), and so on. Here, you are looking at some complex, expensive equipment which also requires a good deal of expertise.

Thin-layer chromatography (TLC) gives you a simple, efficient, inexpensive method of separating and identifying exactly what you have, a simple qualitative analysis and, in many cases, quantitative.

A Horse Race

With TLC, what you have is a horse race. Each horse represents a different molecule (that is, AuCl, PtCl, OsCl, etc.). We start all the horses together, open the gate, off they go, they jockey back and forth at first, then it becomes evident after awhile that some move ahead faster than others. In time, they are separated

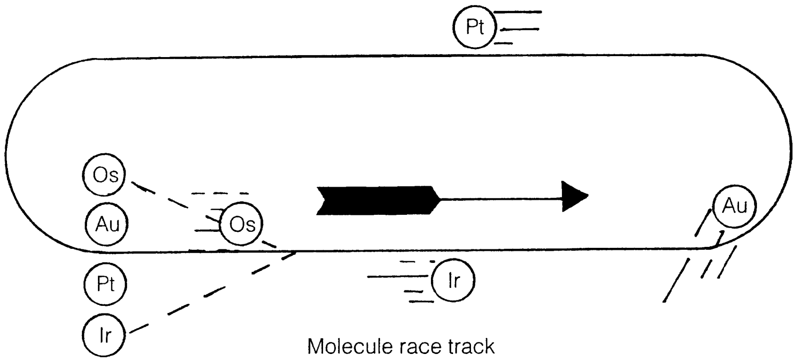


Figure 13.1. Separation of molecules

from one another—strung out, each a different distance from the starting line. If we freeze this picture, we can see each horse by himself and measure the distance he is from the starting line. They are no longer in one blob (bunch), but now are separated. See Figure 13.1.

Which Way to Go

As with many separating methods, there are almost limitless combinations of modes from which to select. This is also the case with chromatography, there are various solvents, sorbents, plates, tanks, developing reagents, ascending, descending, and so on. It can get quite confusing; therefore, I am only going to cover the mode I feel is the easiest, less complicated method for the separation and identification of Au, Pt, Rh, Ir, Ru, and Os from a solvent, along with the various reagents used to develop the separation zones to identify them by color and the R_f values.

Simple Examples in Order to Familiarize the Reader with TLC

Let us start out with a puzzle. We have three identical bottles of water-soluble ink. The color of the ink of all three is the same. The labels are missing.

Two of the bottles of ink are from the same company and brand; one is from a different company and is a different brand. The problem is: Which are twins and which is the odd bottle?

We could approach the problem from many ways: wet chemical analysis and so forth. However, here is where paper chromatography affords us a quick low-tech method of identifying the odd bottle from the twins.

1. We cut out a rectangle of filter paper.
2. Draw a light pencil line 1 in. from the bottom.
3. Spot a sample from each bottle on the line with a micropipet, using the same amount for each, ~ 10 µL. Identify each spot with each bottle (1, 2, and 3).
4. Dry the spotted paper (air dry or in a low-temperature oven). See Figure 13.2.
5. Place about ¼ in. of distilled H_2O in a suitable beaker (a lipless beaker is best), cover the beaker with a glass plate, and leave it covered for 1 h. This is to let the humidity in the beaker reach equilibrium (more on equilibrium later).
6. Fold your spotted paper into a cylinder, stapling the ends together, spots facing out.
7. Place the cylinder carefully into the beaker and cover with the glass plate. See Figure 13.3.

What we are doing is called an ascending paper chromatograph. The paper is called the stationary phase; the water in the beaker is called the mobile phase. The pencil line where we spotted samples 1, 2, and 3 is called the point of origin.

The Race is On

Each ink spot consists of several distinct molecules of different colors which make up the color of the ink (its components). The stationary phase acts as a wick; the mobile phase (in this case, H_2O) moves up the stationary phase (ascending).

The mobile phase in its upward movement passes through our spots of ink. The ink, being soluble in our mobile phase, goes along with it. Now, as the various molecules that make up the ink travel at different speeds in time and

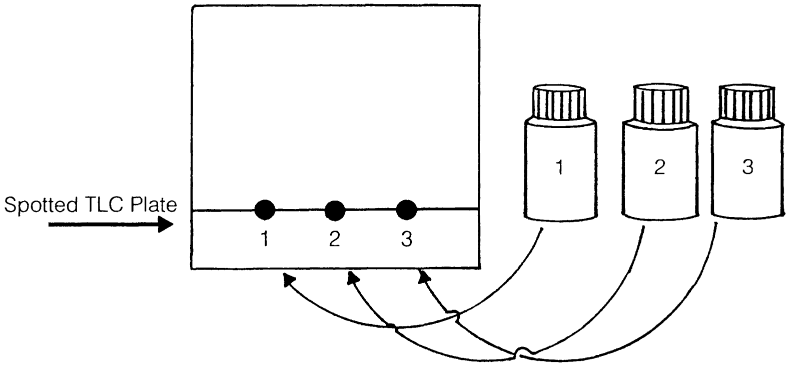


Figure 13.2. Spotting of TLC paper

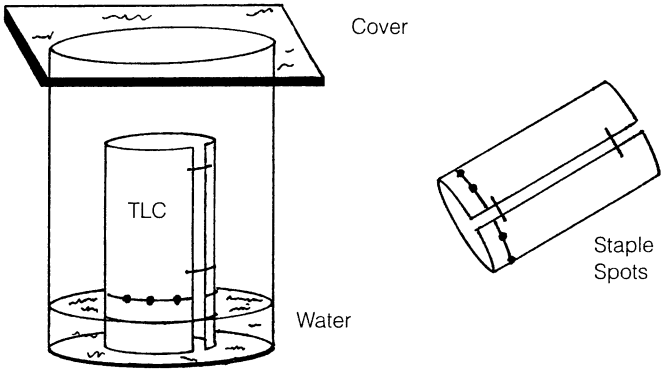


Figure 13.3. Prepared TLC placed in a beaker

distances traveled, they become separated from one another, with enough space between each so that each can be seen alone. See Figure 13.4.

Simply by looking at the separations of the three spots of ink, it is evident which two spots are identical twins made up of the same molecules; they will be exactly alike. The odd ink spot will draw a completely different picture. See Figure 13.5.

In the case of our water-soluble ink chromagraph (picture), our mobile phase is H_2O, our TLC plate stationary phase (adsorbent) is filter paper, and our developing tank a beaker. In our case, simple equipment and a simple procedure provide satisfactory results for the problem.

Taking the Results Further

We could dry our paper chromagraph, cut each individual separation with scissors, and further analyze each by other methods. See Figure 13.6.

Example: Do a TLC on a mixed bag of Au, Pt, and Pd as chlorides. Once you have them sufficiently separated, remove the one you choose, dissolve it in aqua

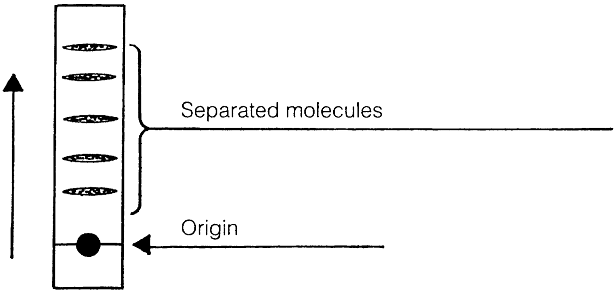


Figure 13.4. Molecules spread apart on TLC plate

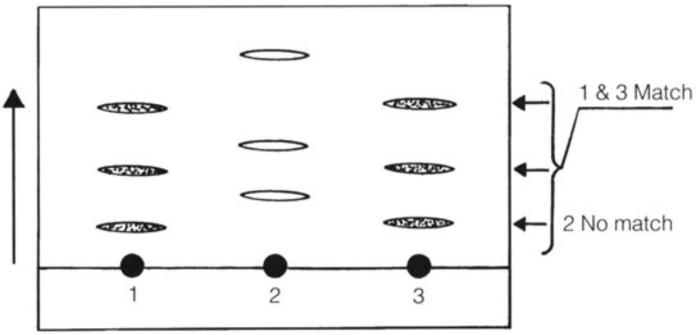


Figure 13.5. Pattern showing which molecules are identical

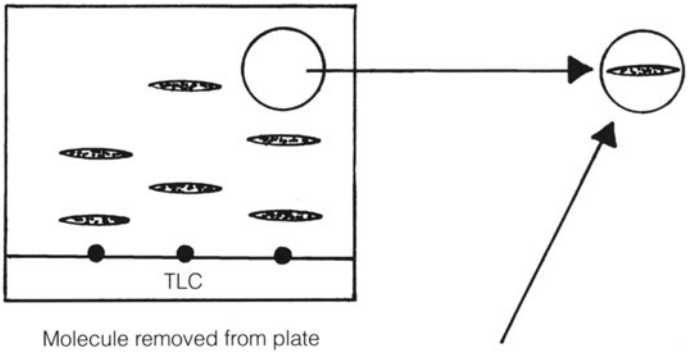


Figure 13.6. Removal of selected molecule for further testing

regia, de-nox, and with the proper reduction reagant, precipitate it as a metallic. At this point, you can weigh the results; by knowing the exact volume you applied to the TLC stationary phase, you can easily determine the exact amount of Au, Pt, and Pd per liter of your starting solution. There are all sorts of evaluation tests that can be done once you have the various molecules separated—dip stick chemistry, assay procedures, ion-exchange resin, spot plate, blow pipe, and so forth.

Stationary Phase

In our ink TLC, the stationary phase was filter paper. The most frequently used TLC stationary phase (TLC plates) consists of aluminum or glass plates coated with a silica gel adsorption layer of various thicknesses. The most common coating thickness of the adsorption layer is 0.2 mm. The sizes of aluminum-backed, silica gel TLC plates run from 5 × 10 cm to a 500 × 20-cm roll. The aluminum TLC plates are used more often than most glass plates for various reasons. They can be cut with a scissors to any size you desire and are not subject to breakage like glass plates. They are also easier to spot with the sample.

Adsorption is a surface phenomenon in which a thin film of gas, vapor, or liquid is held on the surface due to a combination of physical and weak chemical forces. The film of adsorbed species may be only one or two molecules thick. This process differs greatly from that of absorption in which strong chemical bonds are formed (for example, a sponge absorbs water, etc.). The *adsorbent* phenomenon is what allows the molecules to move along in their race and not become immobile and absorbed on the surface. Remember, it is an *adsorbent* surface, not an absorbent surface. This *adsorbent* phenomenon is the basis of any type of chromatography.

There are hundreds of materials that are adsorbents of various activities—some are weak, some medium, some strong. In the group into which they fall depends on the surface area, the chemical nature, and the geometrical arrangement of atoms. The most common used in the strong group are silica gel, fuller's earth, activated charcoal, activated alumina (aluminum oxide), and activated magnesium silicate. Silica gel is probably the most often used stationary-phase adsorbent due to the fact that it is very inert chemically.

Now each and every molecule has a different degree of attraction to the adsorbent. Therefore, as the mobile phase is carrying them upward across the stationary phase (adsorbent surface), each tries to hang on to the adsorbent with a different degree of tenacity; thus, they all travel at a different speed, some moving along fast, others more or less dragging their feet. Therefore, in time they are all separated and strung out, just what we want.

Filter Paper versus Silica Gel Aluminum-Backed Plates

Thin-film chromatography is easily done on filter paper. Watman No. 1 for TLC has a moderate speed; No. 4 is faster; No. 20 is slower. Watman No. 3MM and No. 15 are thicker, but offer no advantages. All of Watman papers can be purchased in sheet or rolls.

Mobile Phase

There are innumerable choices of possible solvents (mobile phase), because TLC is used for analyzing countless numbers of organic and inorganic mixtures of molecules. We are, however, interested only in mixed bags of precious metal chlorides. This fact narrows it down. There is no reason for the reader to get involved in looking for a suitable solvent.

Criteria for Reagents in TLC Work

1. The solvent must be of high purity and purchased from a chemical (reagent) supply house with a repetition for delivering the same reagent of the same purity and assay consistently.

2. It must be reasonably priced.
3. It must be able to do the job intended—that is, displace the solute from the adsorbent in such a manner that the solute is carried in the mobile phase across the plate. This must be done in such a manner that the different molecules will be deposited in different places and can be subsequently identified. This characteristic is called the eluting power.
4. The mobile phase (solvent) must be completely unreactive toward the solutes (our spots) and the adsorbent surface.
5. It must have a low boiling point, as it must be able to evaporate quickly once the stationary phase is removed from the developing tank or beaker.

R_f Value

The R_f value is the distance a spot has moved up the plate (measured in centimeters) from the origin point (our pencil line) divided by the distance moved by the solvent.

$$R_f = \frac{\text{Distance moved by spot}}{\text{Distance moved by the solvent front}}$$

In Figure 13.7 we show two molecules starting out together from the starting line (origin). The solvent moves up the plate separating "A" and "B" from each other. Let us now remove the TLC from the developing tank, let it dry, and develop the separation zones. We see two different colored bands or dots—"A" and "B." If dot "A" moved 5 cm up from the origin and the solvent front moved 20 cm up from origin, we divide 5 cm by 20 cm to get 0.25; this is our R_f value for "A." If "B" moved up 14 cm from the origin, then 14 divided by 20 cm equals 0.7; this is the R_f value of "B." What does this mean? Let us identify "A" and "B" as "A" = gold and "B" = Pt. We know that if we are using the same

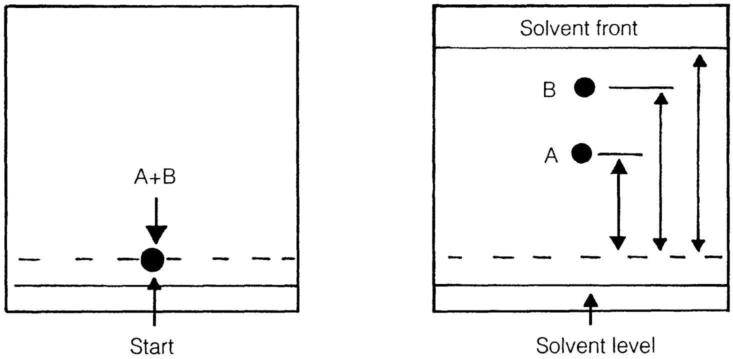


Figure 13.7. Calculating R_f values

solvent in testing a similar solution for values, and we come up with a R_f of 0.25, then this is gold. If we come up with a R_f of 0.25, then this is platinum. Therefore, we have established that any time we use this particular solvent, if we come up with a R_f of 0.25, this spot or separation is gold; a R_f of 0.7 would be platinum. The R_f values change with a change of solvent and composition of spotting material. This will become clear when we get into solvents and R_f values assigned to them.

Visualizing Agents

In a great many cases, once we have developed the TLC, we are unable to see the individual zones, as many of the ions are colorless. In this case, we must spray the developed TLC with a reagent that will color them different colors. Example: We have dissolved a sample of finely ground ore in aqua regia and de-noxed it by boiling it down several times between additions of HCl, to get rid of the HNO_3. To this final test solution we add a 1% (w/v) solution of sodium chlorate, made with distilled H_2O in a volumetric flask to 500 ml. Spot the paper with 0.10-ml aliquots with a pipette in a line approximately 7 cm long on the pencil line (origin line). Let it dry well. If the atmosphere is too humid, dry it in a vacuum dessicator for 40 min; see Figure 13.8. Place the paper in the

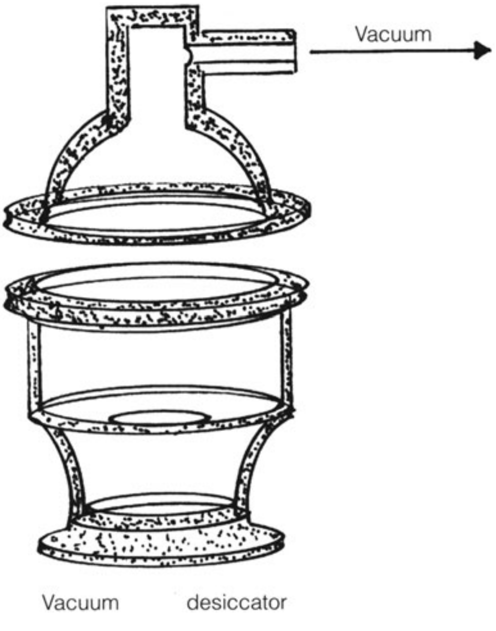


Figure 13.8. Drying spotted TLC paper in a dessicator

developing tank and develop; remove it from tank and let it dry. When dry, spray with a fine mist of fresh stannous chloride solution (SnCl) dissolved in HCl and let it dry. At this point, the zones will be visible as colored bands (that is, Rh = yellow orange, palladium = brown, platinum = yellow, gold = yellow).

NOTE: We added the chlorate to the solution we are testing to convert Pt *II* to Pt *IV* to avoid two different Pt bands.

If we have ions of the same metal in the same solution but in different oxidation states as Pt *II* and Pt *IV,* we are going to get two Pt bands—one for Pt *II* and one for Pt *IV.* However, if we convert all the Pt *II* ions to Pt *IV,* then we have all the Pt ions in one band or spot.

In many cases, the bands are visible under ultraviolet light. However, it is simple to develop the zones with reagents. This is especially useful so you can remove a zone for additional work or isolation. There are both destructive reagents and nondestructive reagents used for making bands visible. A nondestructive reagent is NH_4OH = H_2S + $SnCl_2$ + HCl + $SnCl_2$ + KI + thiourea + HCl + HSCN + benzidine + dianisidine + *p*-nitrosodime-thylaniline sodium thiosulfate.

As we are not interested in destroying the bands or spots, I will not list them. We use the nondestructive reagents because we do not wish to change the composition of our developed bands or spots, in case we wish to remove them separately for further analysis.

Step-By-Step TLC Procedure

The starting material is a mixed bag of metallic ions in HCl (the unknown). The equipment consists of the following:

1. A set of purchased standards which consists of AuCl, PtCl, PdCl, and so forth. The standards are readily available from your chemical supplier. Each bottle carries its assay on the label. See Figure 13.9.
2. A glass TLC developing tank with glass lid. See Figure 13.10.
3. Disposable 10-μL micropipettes (capillary tubes) for spotting TLC plates. See Figure 13.11.
4. Some aluminum-backed silica gel TLC plates, 20 × 20-cm; layer thickness, 0.2 mm. See Figure 13.12.
5. Mobile phase reagent consisting of seven volumes of acetone, two volumes of distilled H_2O, one volume of HCl + 2 g of thiourea. This mobile phase works very well for Au. Pt, Pd, Ir, Rh, Os, and Ru. Keep in a dark, stoppered, glass bottle in a cool, dark place.

   Using the above mix of acetone, water, HCl, and thiourea, and using R_f values to identify the individual spots, the published values are Ru = 0.21, Ir = 0.44, Rh = 0.64, Pd = 0.93, Os, and Au, Pt = 1.0. My second

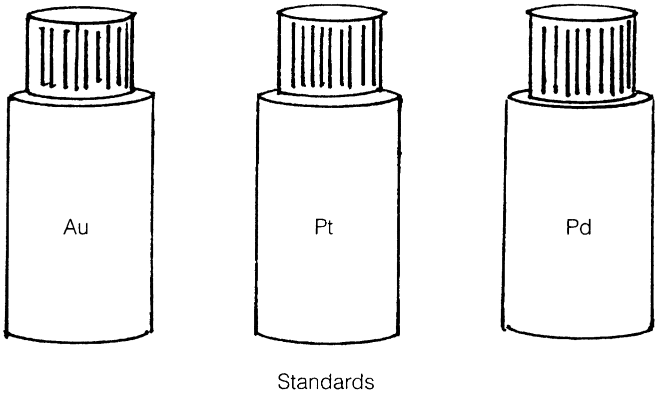


Figure 13.9. Purchased standard solutions

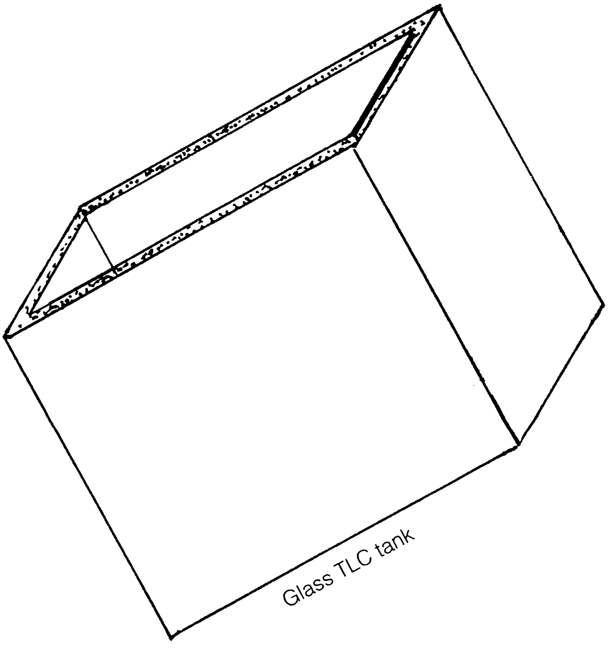


Figure 13.10. TLC developing tank

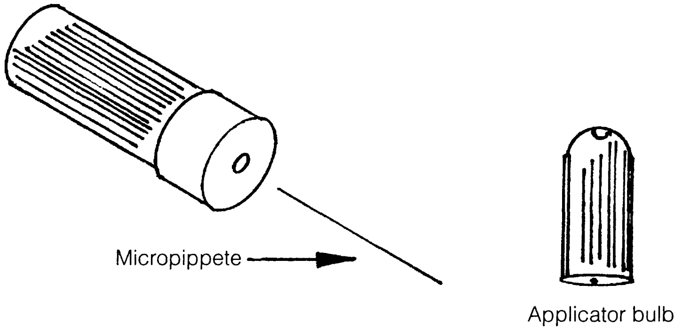


Figure 13.11. Micropipette to spot TLC plates

choice for a mobile-phase reagent would be an 0.1 *M* NaCl solution (salt water). In this case, you must use chemically pure NaCl (no iodine). In using this mobile-phase reagent, the R_f values (published) are Au = 0.49, Pd = 0.78, Os = 0.8, Ru = 0.85, Rh = 0.89, Pt = 0.93, and Ir = 0.99.

NOTE: An 0.1 *M* NaCl solution is prepared by dissolving 5.9 g of pure NaCl in distilled H_2O and diluting to 1 L, using a 1-L volumetric flask. See Figure 13.13.

6. Reagents used to develop spots or zones. The ions that we are dealing with have an intrinsic color (by their nature)—that is, Ru is brown, Os is brown, Rh is red, and Ir is brown, but only in the presence of an oxidizing agent (HNO_3, H_2O_2, etc.).

   Platinum is orange, as the intrinsic colors of Pt is yellow and Au is yellow. Here, we have three ions which are brown, one which is red, one which is orange, and two which are yellow. Therefore, to prevent confusion when visually identifying each metal zone, we can use various reagents to change the intrinsic colors to different colors for each identification. Example: We have say three zones, 1 orange, 2 yellow, yellow

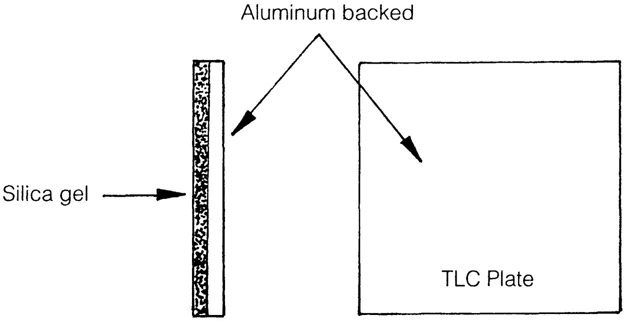


Figure 13.12. TLC plate

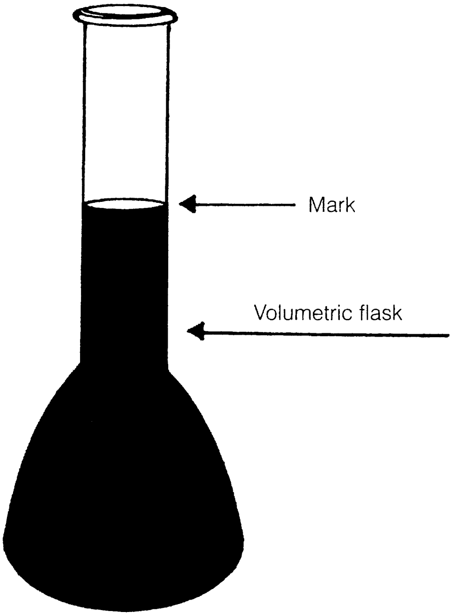


Figure 13.13. Standard volumetric flask

in color, the intrinsic colors of Pd, Pt, and Au, respectively. Now, if we spray these three zones with a solution of tin chloride to which we have added a few crystals of potassium iodide, the zones are now brown (Pd), yellow (Pt), and violet (Au) in color. Therefore, you have many directions you can go with various color-changing reagents. Let us look at some of them.

Ru: Intrinsic color is brown—spray with thiourea and HCl solution, it is light blue; with dianisidine, it is yellow brown, and with sodium thiosulfate, it is pink.

Os: Intrinsic color is brown—spray with thiourea and HCl solution, it is red.

Rh: Intrinsic color is red—spray with benzidine, it is brown.

Ir: Intrinsic color is brown—spray with benzidine, it is blue.

Pd: Intrinsic color is orange—spray with p-nitrosodimethlaniline, it is bright yellow.

Pt: Intrinsic color is yellow—spray with benzidine, it is brown.

Au: Intrinsic color is yellow—spray with $SnCl_2$ + KI, it is violet.

7. Spray bottle capable of providing a fine mist used to spray developed TLC plate for visual identification (reagents to change ion's color); see Step 6. See Figure 13.14.

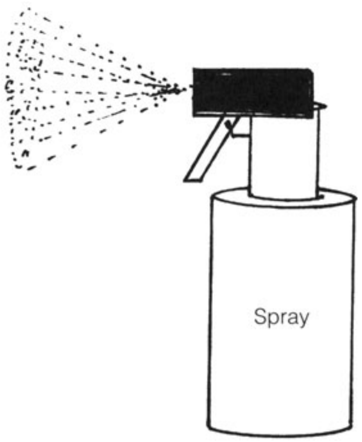


Figure 13.14. Color-developing spray bottle

8. Low-temperature electric oven with good temperature control for drying the TLC plate after spotting it, drying after removing the TLC plate from developing tank, and again after spraying it with chosen reagent to develop spots or zones.
9. Centimeter scale to measure the spot's or zone's final resting place from the origin, and the distance from the origin to the solvent front to calculate the various R_f values.

Operating Procedure

1. Draw a light pencil line 1 in. from the bottom completely across the adsorbent face of a new TLC plate. This is our origin line.
2. Make a paper map showing our origin line, space out four numbers. Let 1 = Au standard, 2 = Pt standard, 3 = Pd standard, and 4 = unknown. Now spot the TLC plate according to our map, using a disposable pipette for each. (See Figure 13.15.) Air dry or oven dry the spotted plate.
3. This next step is very important. Put enough mobile-phase reagent into the developing tank to come up about ¼ in. on the plate; place the lid on the tank. See Figure 13.16.

   At this stage, regardless of what reagent you use as a mobile phase the tank must remain closed for at least 1 h or more, prior to placing your TLC plate into the tank for developing.

   This 1 h or more with the mobile phase in the tank with the lid on ensures that the atmosphere in the tank is saturated with respect to the solvent vapor. Failing to saturate the internal area of the tank completely prior to putting the TLC plate in the tank for developing will result in

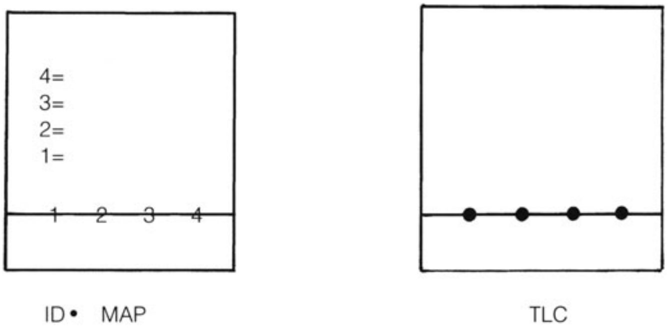


Figure 13.15. Map of spotted TLC plate for reference

the mobile phase moving up the stationary phase (the plate) and evaporating from the plate in an effort to saturate the tank. The higher it goes up the plate, the more it evaporates, giving you a strange outcome in which there is no way you can establish R_f values or correct matching of spot columns. See Figure 13.17.

4. Once you have satisfied yourself that the tank containing your solvent (mobile phase) has remained closed long enough and is completely vapor saturated (reached static equilibrium), you are ready to put your TLC plate in the tank, close the lid, and let the TLC develop.
5. When developed, remove the TLC plate and dry in the oven; just enough light heat to dry it, do not cook it.

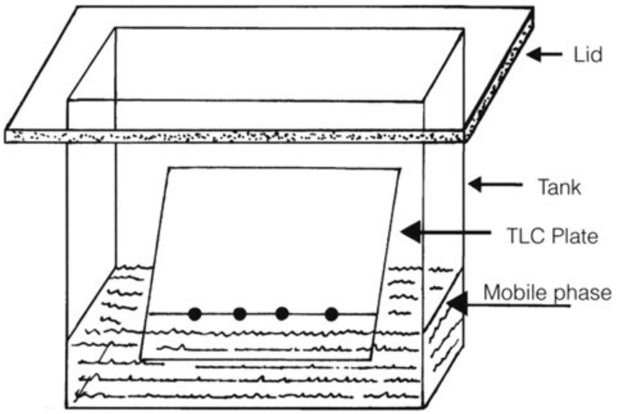
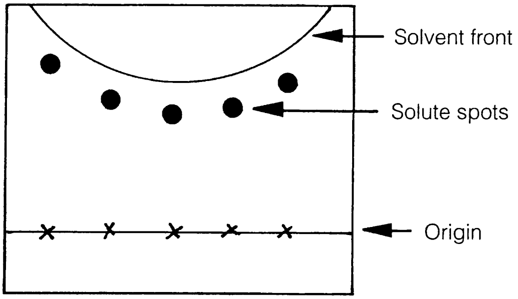


Figure 13.16. Allowing tank to reach equilibrium with mobile phase prior to putting TLC plate in for development



TLC from unsturated tank

Figure 13.17. TLC plate results when placed in a tank that has not reached equilibrium

6. Spray the plate with your reagent to develop the zones.
7. Dry again.
8. At this point, you can calculate the R_f values and compare them with the published R_f values for the mobile phase used. Compare these numbers with the R_f values you get for the standard zones.

Let us assume that you used a 1 *M* NaCl solution as your mobile phase, and SnCl + KI spray to develop the zones. If you did everything correctly, your Au standard zone should be a violet color with a R_f value of 0.49. Your Pd standard zone should be a brown color with a R_f value of 0.78, and your Pt standard zone should be a yellow color with a R_f value of 0.93. Any Au, Pd, or Pt in your unknown spot should be lined up—Au across from the Au standard, Pd across from the Pd standard, and Pt across from the Pt standard. The colors should also be correct.

Practice with standards over and over until you can repeat the published R_f values accurately every time against the published R_f values given for the two mobile phases given in this chapter. Once mastered, you can dispense using standards for the most part and nail down your qualitative assays with confidence. As we used a nondestructive visualizing reagent at Step 6 to develop our zones (that is, $SnCl_2$ + KI which made the zones come up Au violet, Pd brown, and Pt yellow), we can carefully remove each zone separately by scraping it off the plate, or in the case of a filter paper TLC, cutting it out.

Thin-film chromatography is widely used in inorganic chemistry to analyze various solutions for the presence of a particular molecule. For example, if we have something that we think contains barbiturates, we simply run a TLC, then spray the zones with *S*-diphenylcarbazone, which is the destructive visualizing agent for barbiturates. If we come up with a zone of purple spots, we have barbiturates.

I am pointing this out so that you can relate it to dip stick chemistry, as most indicator papers contain destructive visualizing reagents in their makeup. For the most part, all types of chromatography are related to paper chromatography. The Chinese did it with chalk way back when. It is the basis of DNA matching and so forth.

14

Dip Stick Chemistry

Indicator Strips, Test Papers

Both man and beast are engaged in a continuous game of testing. If one were to think about it, you would be quite surprised at just how many times a day you are involved in directly testing something consciously or unconsciously.

A great many of your daily tests require no special equipment, devices, or reagents to perform other than your senses. For example, you check the temperature of the baby's milk via a drop or two on your inner wrist, you test the bread or cake to see if it is cooked, the old toothpick test; of course, here your instrument is the toothpick. I am sure that if you gave it some thought, you could come up with hundreds of tests.

Today, in addition to litmus and pH tests, there are other test papers, dyes, and indicators to test just about anything you desire.

Although this book is mostly concerned with precious metals and reagents, there are countless other metals and reagents which you must know about in order to carry out various reactions, precipitations, and so forth.

For example, in many cases if you have precious metals in a solution which contains certain other ionic species which would interfere with the successful precipitation, reaction, and so forth of the desired metal or metal salt; here is where dip stick chemistry comes to the forefront. Often it is impossible to precipitate gold from a chloride gold solution due to the presence of NO_3 ions. A quick check with a test paper strip for the determination of NO_3 will pinpoint your problem.

Recovering Ag from photographic solution? Ready to neutralize solution and dump it? Simply check it with an Ag fix stick. This will tell you how many grams of Ag per liter, if any, are left in the solution and at what pH.

You can go through the front door—check the solution before you start to recover the Ag. To start out, say your Ag fix stick shows you have 10 g/L of Ag (or 1¼ ounces per gallon). If you strip out 1¼ ounces per gallon, you know where you are.

Regardless of what you call them—test papers, test strips, test sticks, indicators, and so forth—I will call them dip sticks. You will find that in all chemical systems (medical, organic, inorganic, etc.), there are dip sticks available for that field, along with many which cross over. Actually, there are hundreds, from sugar in urine to water in gasoline and some for gasses. I will cover those dip stick indicators here which I feel would be most useful to the task at hand.

Some dip sticks for certain ionic species require special treatment to mask various ions which, if not masked, would give a false indication. When purchased from your vendor, this information comes with the dip sticks. In all cases, if you have a single ion in solution alone, this reduces the problem of identification to the minimum. A mixed bag of ions in solution can represent a more complex solution to the identification of a single ion species in the soup, but not always.

A Few Available Useful Dip Sticks

Aluminum: Determination of Al ions in the range 0–500 mg/L; color changes from pink to red.

Ammonium: Determination of ammonium ions in the range 0–400 mg/L; color changes from yellow to orange.

Ascorbic acid: Determination of vitamin C in the range 0–2000 mg/L; color changes from yellow to green-blue.

Chlorine: Determination of chlorine ions in the range 0–100 mg/L; color changes from white to red-violet.

Chromate: Determination of chrome oxides in the range 0–500 mg/L; color changes from pink to violet.

Cobalt: Determination of cobalt ions in the range 0–1000 mg/L; color changes from white to greenish blue.

Copper: Determination of Cu^+ and Cu^{2+} in the range 0–1000 mg/L; color changes from white to red-violet.

Cyanide: Determination of CN in the range 0–30 mg/L; color changes from white to red-violet.

Iron: Determination of Fe ions in the range 0–1000 mg/L; color changes from white to dark red. Iron also comes in strips with a range of 0–500 mg/L; color changes from white to blue-violet.

Nickel: Determination of nickel ions in the range 0–1000 mg/L; color changes from white to light red.

Nitrate: Determination of nitrates in the range 0–500 mg/L; color changes from white to red-violet.

Nitrite: Determination on nitrites in the range 0–50 mg/L; color changes from white to red-violet.

Peroxide: Determination of peroxide in the range 0–50 mg/L; color changes from white to blue. Peroxide dip sticks also come in a range of 0–100 mg/L; color changes from white to blue.

Phosphate: Determination of phosphates in the range 0–100 mg/L; color changes from white to bluish green.

Potassium: Determination of potassium ions in the range 0–1500 mg/L; color changes from yellow to orange.

Silver: Determination of silver in photographic solutions (semiquantitative) in the range 0–20 mg/L; color changes from cream color to salmon with purple-red dots.

Sulphite: Determination of sulphites in the range 0–1000 mg/L; color changes from white to salmon.

Tin: Determination of tin ions in the range 0–500 mg/L; color changes from white to dark blue.

Zinc: Determination of zinc ions in the range 0–100 mg/L; color changes from orange to red.

As you see, these dip sticks are not only qualitative but also quantitative. Each package comes with instructions for use, masking if required, and a color chart to compare color of the stick against the chart to determine the milligrams per liter. In most cases, you dip the stick in the solution in question, compare it against the color match chart, and you have the answer.

If you have a good selection of dip sticks on hand, you will find them indispensable and a great time saver to head you in the right direction.

Dip sticks are available for the detection of hundreds of items and reagents. The following is a short list, some which might interest you: alkali sulfites, ammonia, blood, borates, boric acid, chromate, diazotization end point, disinfectants, halogens (free), halides, HOH, HOH in butter, hydrogen sulfide, hydrogen fluoride, hydrocarbons, hydrosulfite, iodides, iodine (free), lubricating oils, mastitis, relative moisture, oxidizing agents, peroxidase, peroxide, phosphatase acid, phosphate, quaternary ammonium compounds, reducing agents, sperm, steel, and nondestructive for Co, Cr, Cu, Pb, zirconium, and so forth.

Stains, Dyes, and Indicators

There are hundreds of these available for all sorts of uses; an example is Methylthymol Blue. This is a water-soluble dye used for the determination of zinc. There are 50 dyes available on the market as pH indicators, each confined to a given range—that is, Malachite green range 0–2 pH, color changes from yellow to green from a pH of 2 to a pH 11.5, no change from 11.5 pH to 14 pH. It kicks in again to go from dark blue to colorless. 4-Nitrophenol is a very short-range dye from a pH of 5.5–6.75. It goes from colorless to yellow. These dyes are extremely useful when tracking the pH of a solution looking for a certain pH.

The vast number of dyes available are the foundation on which dip sticks are manufactured. A good handbook on stains, dyes, and indicators will be found to be extremely useful in more ways than you can imagine.

15

Solvent Extraction

Solvent extraction (SX) is a system whereby you can transfer selectively certain ionic species in an aqueous solution to an organic solvent. This system is also referred to as liquid/liquid extraction or separation. The solvent extraction reagents can be cationic, anionic, or neutral, depending on what you wish to isolate or collect in the solvent.

The SX system is very useful; however, sulfate solutions are a tough nut to break. There are some important exceptions. What you wish to accomplish is to strip out of solution the ions that you wish to capture minus the ones you wish to leave behind. Therefore, separate the two solutions and remove what you want from your solvent, cleave the bond and drop out your product.

What happens is that the metal of interest reacts with your solvent to form a chemical compound which is much more soluble in the organic phase.

Once we have the metal we want captured in our organic phase and have separated it from our inorganic phase, we must at this point introduce a reagent which will cleave the bond, precipitating the metal. Now we have our metal M° and our original solvent ready to use on the next SX. In some cases, you must clean your solvent of impurities (by scrubbing distilling).

For precious metals, neutral and anionic extractants are used most often. When done correctly, they produce a fine high-grade product, 0.999+ with little loss of solvent. The amount of solvent you lose depends on how sloppy your setup is. You will lose some normally, and as most organic solvents are rather expensive, you wish to keep this loss at a minimum. A 4% loss of solvent can be tolerated. SX, in the simplest terms, is liquid ion exchange.

Some Organic Solvents in Use Today

The following list is far from complete; there are hundreds more.

Water
Carbon tetrachloride
Benzene
Carbon disulfide
Dibutyl ether
Diethyl ether
Nitrobenzene
Tributyl phosphate—selective for Pt
Chloroform
Dibutyl carbitol—selective for Au
di-*N*-Octylsulfide—selective for Pd
Dimethyl sulfoxide (DMSO)

Dimethyl sulfoxide (DMSO) which can be purchased in many health food stores is a very dangerous solvent. It is touted as a relief for joint pains and so forth. This comes from the fact that some veterinarians use it as a rub for sore joints on horses. Because DMSO is a powerful, powerful solvent, if rubbed on the skin over the affected area, it will put any and all bacteria and so forth present on the skin into solution, thus carrying all the junk directly into the blood. This could result into a nice infection, or worse.

SX to Purify a Metal

We will use gold as an example. The gold in question is somewhat below specification and we wish to raise it to a purer state. We can accomplish this in many ways: pyro methods or oxidizing of the base metals, including any small amounts of Pt. We can digest it in aqua regia de-nox precipitate with SO_2, then repeat this process until we reach the desired purity. Reduce the unwanted base metals to chlorides by spurging the molten gold with Cl_2 gas (Miller process). We could upgrade the purity by simple dilution with enough fine gold, provided you have sufficient fine gold on hand.

With SX you have less operations and come out with a high-quality product: dissolve in aqua regia, then de-nox, take the precious metal chloride solution and take the cations of Au up in dibutyl carbitol, and scrub out any base metals (that went up in the carbitol) out of the carbitol with dilute HCl. Separate and drop the gold out with oxalic acid as a high-purity gold sand. See Figure 15.1.

Very Old Method of Purifying Placer Gold Flakes and Small Nuggets

This is solvent purification of sorts. Here, a mixture of ⅓ NaCl, ⅓ NH_4Cl, and ⅓ brick dust or old broken pottery dust was mixed well. A layer was placed in

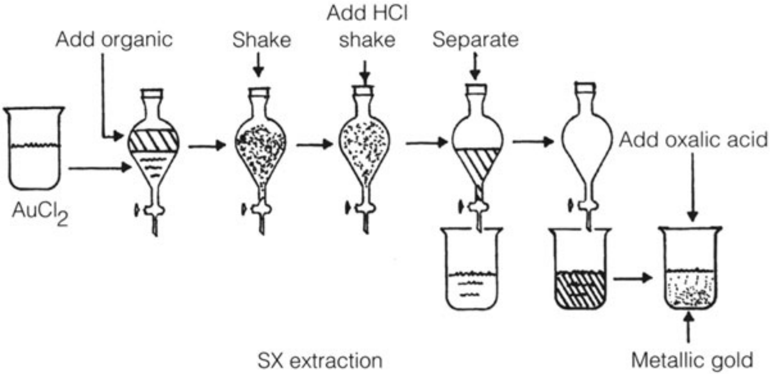


Figure 15.1. SX flowchart

the bottom of a crucible. This first layer was leveled out and tamped down firmly but not too hard. Gold flakes and placer nuggets were then placed on this layer, but not touching each other, as best as possible. Then ½ in. of the NaCl, NH_4Cl, and brick dust mix was placed on top of the gold layer, tamped level, and more gold added. This procedure is repeated until you are within 1 in. of the crucible top. This 1 in. is now covered with the mix, pressed down firmly, and the crucible covered with a crucible cover and luted with fire clay. The refining mix is ⅓ NaCl, ⅓ NH_4Cl, and ⅓ brick dust by volume.

The packed and luted crucible is then placed in an oven (or assay furnace). The temperature is brought up to just below the melting point of gold (1700°F) and held there for 1–2 h.

You do not want to melt anything, just cook it. What happens here is simple. The NaCl and NH_4Cl reduces the base metals to chlorides, actually leaching them out of the gold. These base metals are absorbed by the brick dust. Break this material and pan off the lights. What is left is almost pure Au sponge. See Figure 15.2.

Parks System

This is a very old and reliable SX system in which galena was reduced to crude metallic lead. This lead contained impurities such as copper, antimony, arsenic, gold and silver.

In 1850, Alexander Parks of Birmingham, U.K., patented his SX system—a liquid/liquid/liquid method of removing the silver and gold. The process is called Parks desilvering method.

First, the lead was refined to remove the copper, antimony, and arsenic (impurities). This gives up pure lead, with the impurities consisting of Au and Ag. See Figure 15.3.

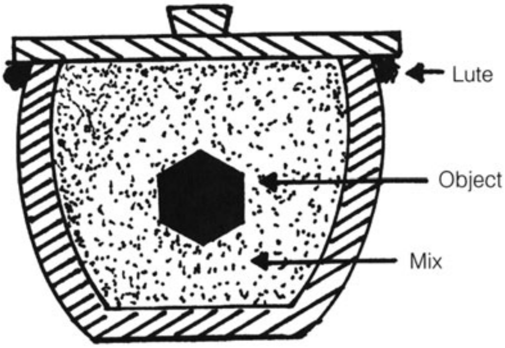


Figure 15.2. Section through depletion plating setup

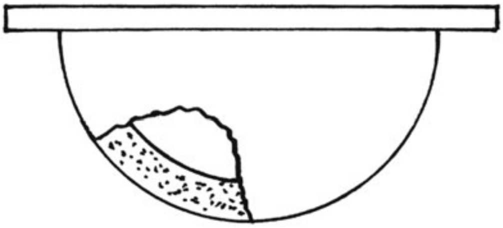


Figure 15.3. Cast-iron melting pot used to refine lead by the Parks method

This initial refining is done by skimming the molten lead at various temperatures. First the lead is heated slowly to a point just above its melting point. Any copper at this point is not molten, but being lighter then lead, it will float to the top as a copper dross, where it is easily skimmed off.

Antimony and arsenic is removed by the same method, the only difference being that this is carried out with the molten lead at a good red heat, leaving behind pure lead containing silver and perhaps some gold.

Liquid/Liquid or SX Separation of Silver and Gold from Molten Lead

Zinc melts at 419°C = 786.2°F

Lead melts at 327.4°C = 621.32°F

The specific gravity of zinc is 7.14.

The specific gravity of lead is 11.35.

Zinc has a great affinity for gold and silver—much, much greater than lead.

Taking the data shown above, we have a classic situation for easy liquid/liquid (SX) extraction or separation of Au and Ag from liquid lead. Zinc, in this case, is our solvent, which we use to absorb the Au and Ag from the lead into the zinc and removing the pregnant zinc from the lead.

It is quite simple and straightforward. Zinc melts at a higher temperature than lead. Therefore, if we have a molten mixture of lead and zinc both at a temperature above the melting point of zinc and we lower this bath (mixture) down below the melting point of zinc, the zinc will solidify (the lead will remain as a liquid). Because the zinc is lighter than lead, it will float to the top where it can be skimmed off. This type of separation is called liquidation separation. This is possible because the melting point spread between zinc and lead is 164.8°F. Zinc's affinity for gold and silver being so much greater than lead, when we add molten zinc to molten lead (containing Au and Ag) which is at a temperature above the melting point of zinc, the zinc grabs onto the Au and Ag present in the lead.

Now we have the Au and Ag locked onto the zinc; all we have to do is our liquidation. Bring down the melt (Pb, Zn, Au, Ag) slowly; when you reach the solidification point of the zinc just below 786.2°F while keeping the lead above 621.32°F, up floats the values. Recovery of the values from the zinc skimmings can be accomplished either by retorting off the zinc or taking the zinc up in H_2SO_4 or dilute HCl.

SX Extraction of Gold from a Mixed Bag of Metals in an Acidic Solution

The most frequently used organic solvent for liquid/liquid or SX extraction of gold is dibutyl "carbitol." Carbutik is the registered tradename of Union Carbide Corp. for diethylene glycol dibutyl ether. The reason for this choice is as follows: carbitol is highly selective for gold and is also quantitative. Gold can be recovered by reduction in situ of a high quality. Carbitol has a low volatility, a boiling point of 254.6°C, a high flash point of 118°C, and a low solubility in H_2O at ambient temperature (0.3% at 20°C). Carbitol is recycled over and over with little or no deterioration of its performance or its ability to extract Au from chloride solutions. You can load 25 g of gold per liter of carbitol. (Carbitol will not extract PMGs).

The starting organic phase for SX extraction of gold is 10% carbitol, 15% tridecyl alcohol in kerosene, and about 20% aromatic content.

SX for Au Step by Step

Step 1. The first step is to make a feed solution. Your primary or secondary material must be put into an ionic solution (HCl). This is accomplished by digesting the material in aqua regia, HCl, or Cl_2, your choice. This digestion puts the Au, Pt, and Pd into solution, which gives you gold chlorides, platinum chlorides, palladium chlorides, and various base metal chlorides (that is, iron chlorides, copper chlorides, etc.).

This leaves you with an insoluble gangue. If you have any Ag, Rh, Ru, Ir, Sn, Te, Sb, As, Bi, Pb, and so forth, it will be in the gangue and can be recovered later by other processes. Any Ag and Pb in your starting material will be in the form of silver chloride mud and lead chloride mud. These two are easily removed. Hot water will take up the lead, as it is soluble in hot water, whereas silver chloride is only slightly soluble. The silver chloride is very, very soluble in NH_4OH, making it easily extracted.

Step 2. The carbitol and pregnant chloride are placed in a separatory funnel in equal volumes and shaken vigorously. Now, if our HCl solution from which we are extracting the gold ions into our organic phase (solvent) has a nitric acid content not exceeding 0.1 *M,* we are in good shape. It is very important that the solvent and our pregnant solution are intimately mixed.

Step 3. The separatory funnel is now placed in a ring stand, at rest to allow the two phases to completely separate. The solvent solution carbitol contains the Au on top and the HCl solution on the bottom.

Step 4. Once the separation of the two phases is complete, we carefully drain off the bottom phase into a suitable beaker. All that remains in the separatory funnel is the gold-containing organic phase. In the beaker, we have a HCl solution with the Au removed. This solution now contains various metallic ions (that is, Pt, Pd, Ir, Fe, etc.), depending on what was taken up by the aqua regia solution at the first digestion. We will deal with this later.

Step 5. This step is very important in order to produce a good pure Au product. With the gold in the carbitol, we have some minor amounts of base metal ions, which must be removed. This operation is called scrubbing. Make a 1.5 *M* solution of Hcl (dilute 123 ml of 37% HCl to 1 L with distilled H_2O.) Add an equal volume of 1.5 *M* HCl solution to the carbitol in the separatory funnel. Here again, we go through the Step 2 vigorously shaking routine, let the solution separate as in Step 3, and remove the scrub as in Step 4. Add this scrub HCl solution to the beaker solution.

What the 1.5 *M* HCl solution does is pick up any stay base metal ions in our organic phase, thus removing them. How many times you should scrub the organic phase with 1.5 *M* HCl depends on how much "trash" followed the Au ions into the organic phase in the first place. However, in most cases, one good scrub should do the trick. The final answer is how pure the gold is that you recover as metallic gold from the organic phase.

Step 6. Recover the gold from the organic phase as gold metallic granules (sand).

The loaded carbitol is transferred into a boiling flask, heated not to exceed 90°C (194°F), and stirred with a simple propeller. The reagent used for reduction to metallic gold is an aqueous solution of CP oxalic acid. The reaction is $3(COOH)_2 + 2HA{\cdot}AuCl_4 \rightarrow 2Au^{\circ} + 6CO_2 + 8HCl$.

You should use a little more oxalic acid than the stoichiometric amount to ensure complete stripping of the carbitol. The $6CO_2$ coming off can be handled with a reflux condenser. The operation of gold recovery takes time, anywhere from 2.5 to 3.5 h. The recovered Au is filtered off and washed with 1.5 *M* HCl, and then washed with alcohol to remove all traces of organics.

Because gold is easily reduced from the carbitol solution by any number of reagents, you can, if you choose, use one of these other than oxalic (that is, SO_2, H_2S, rongalite, dektol, hydroquinone, etc.). The stripped carbitol is reused for the next batch.

SX Organic Reagents for Recovering Platinum and Palladium from HCl Solutions

For platinum, you use as an organic phase TBP (tetrabutyl titanate). For palladium, you use as an organic phase di-*N*-octylsulfide. These reagents are used quite similar to the carbitol scrub with 1.5 *M* HCl.

The palladium is stripped from the organic phase with aqueous NH_4Cl which precipitates $Pd(NH_4)_2Cl_2$ (palladium ammonium chloride) and is easily reduced to palladium metal by heat.

Platinum recovery from the TBP is as follows. After scrubbing with HCl, it is stripped with H_2O and the Pt is recovered as $(NH_4)_2PtCl_6$ with ammonium chloride [$(NH_4)_2PtCl_6$ + heat → Pt metal].

A Unique Patented SX Process: U.S. Patent 5284633 Invented by D.L. Gefyer, Pub. 8th Feb. 1994—Sherex Chemical Co. Inc.

In this case the organic phase uses 7-substituted-8-hydroxyquinolines. The claim is that with this organic phase, all the gold and platinum metals are relatively free of base metals. The organic phase which chelates with the precious metals is quite stable and the base metals are easily removed by aqueous scrubbing. As in the above examples of SX, kerosene and tridecyl alcohol are used as the organic carrier. The values are precipitated with an acidic thiourea solution. There is a great amount of research and development going on in SX.

16

Magnetite

Loadstone (Fe_3O_4), also known as iron ore and magnetic, is a black mineral, 72.4% iron submetallic, and readily recognized by its strong magnetic attraction. In a powder form, it is soluble in a 20% by weight of hydrochloric acid; at 1538°C, it decomposes to ferric oxide—specific gravity of 4.9–5.2.

Placer Black Sands

There are numerous deposits of magnetite black sands worldwide. The presence of black sands often indicates the presence of free gold and free platinum. Prospectors look for these deposits, both wet placers and desert dry placers, and set up their jigs, rocker boxes, and so forth, or simply pan.

U.S. Geological Survey Bulletin 1660

This bulletin is a study on precious metal values encapsulated in grains of magnetites (black sands). The bulletin is quite interesting, with lots of micrographs showing the values.

It is available and I recommend reading it, if only for your own amazement. It is stated that the magnetites from placer deposits in the Goodnews Bay District of Alaska will run as high as 1100 PPM (35.37 troy ounces per ton). These PGM values are locked in the magnetite lattice and represent a valuable resource lost during extractive metallurgy. In Chapter 11 entitled "Black Sands," we were concerned with the recovery of free values in the black sands.

After the recovery (if any) of the free precious metal values in our black sands (via sluice, etc.), we wind up with mountains of magnetites. Now the U.S. Geological Survey states that these magnetites have encapsulated in their matrix as much as 35+ ounces per ton. This leaves us with the problem of recovering them and at what cost. There is to date no economical method that I know of or have seen. What is missing in this scenario? Simple, good, clean, high-grade magnetites are very valuable and have many uses. By various reduction and oxidation procedures, magnetite can be converted into various colored iron oxides for use as pigments for paint, cement, plaster, and colored fillers for the plastic industry and so forth. The oxide and oxide pigment business is a very lucrative, high-volume business.

Iron Oxides

There are 13 iron oxides, oxyhydroxides, and hydroxides commercially produced. All your iron oxides and hydroxides consist of FeO and/or OH. The main difference in their composition is the valance of Fe and in their crystal structure: magnetite, maghemite, hematite, and ferrihydrite.

Oxides run the spectrum in colors—bright yellow, orange, bright red, browns, black, even green (green rusts are not oxides in the strict sense; they are hydroxides).

Various oxides of all colors have been used as pigments for artists and decorators since prehistoric times. The cave drawings at Lascaux in France attest to their color, opacity, and light-fastness staying power over long periods of time. Artists from ancient times to the present time still use venetian red, yellow ochre, sienna, and burnt sienna. These can be found in your local art store still today.

The system described here is called the Höganäs system because it originated in Höganäs, Sweden, where it is still been used since its inception there in 1911, some 85 years ago. In the simplest terms, the magnetite is reduced to metallic iron by reducing gas produced by burning coke, which in this case must rob the oxygen from the magnetite to be oxidized to carbon monoxide. The reduction is carried out in silicon carbide flanged cylinders. See Figure 16.1. It can, however, be done in straight-sided silicon carbide crucibles (Figure 16.2).

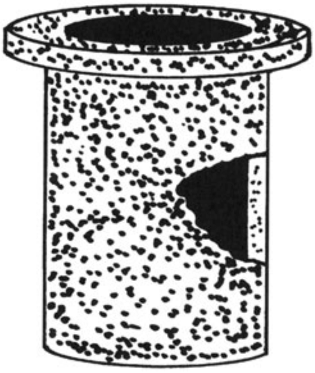


Figure 16.1. Silicon carbide sagger used in the reduction of magnetite to metallic iron

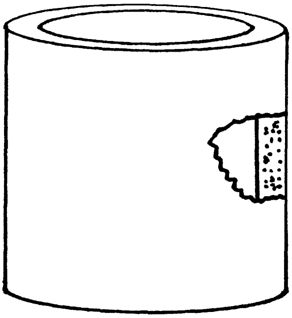


Figure 16.2. Crucible used for reduction of magnetite to metallic iron

The coke used is called breeze, which is fine coke and is extremely cheap and available. The reduction mixture material consists of a coke breeze, fine limestone mixture. The purpose of the limestone is to absorb sulfur in the coke during the reduction.

In order to charge the saggers or a crucible, you must have two concentric sheet metal tubular sleeves of the proper size and length. Each sleeve has handles by which they can be removed after charging the sagger or crucible (Figure 16.3). When in place, the sleeves divide the sagger into three annular spaces (Figure 16.4). The outer and innermost space is filled with coke breeze and limestone mixture. The remaining space is filled with the magnetite; see Figure 16.5.

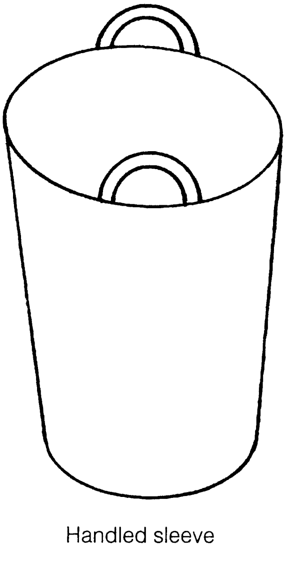


Figure 16.3. Handled sleeve used to separate zones of Fe_2O_3 and coke in the sagger

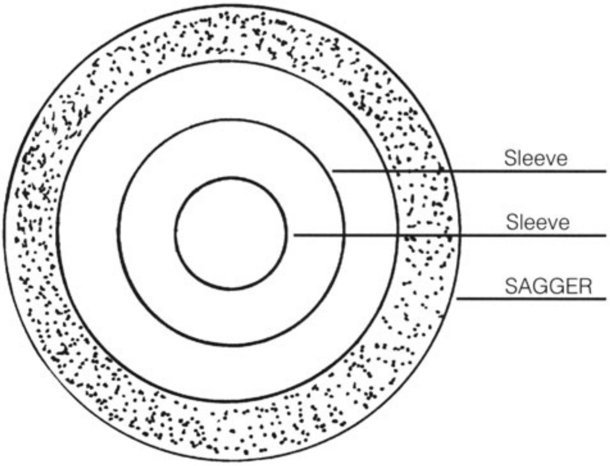


Figure 16.4. Top view of sagger with sleeves in place, sagger ready to charge

Charged saggers can be stacked four or more in height on a small rail car or a steel pallet and run into an oven. See Figure 16.6.

There are many methods to synthesize iron oxide pigments. It is a very large tonnage industry. These operations require large amounts of black sands as feedstock. Therein lies a market for your tabled black sands. The pigment business is not one that can be operated on a small scale. Sell your black sands. Also, the chemistry of pigments is quite complicated and involved. When prospecting for gold and other metals, one should keep an eye pealed for natural deposits of

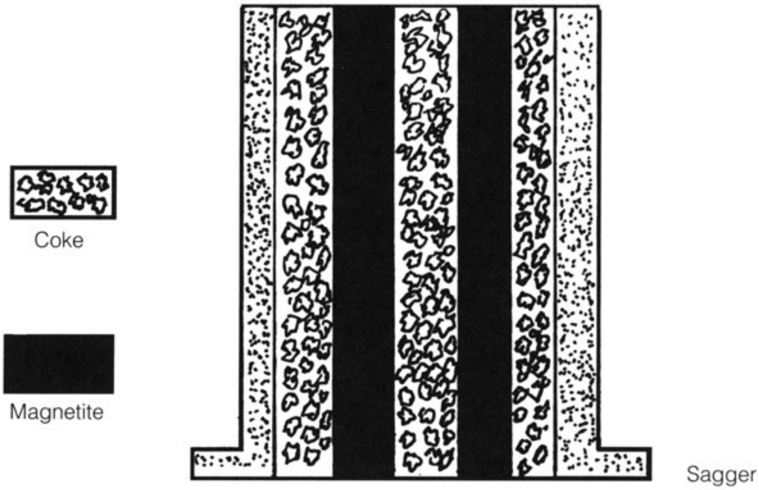


Figure 16.5. Cross section of a charged sagger

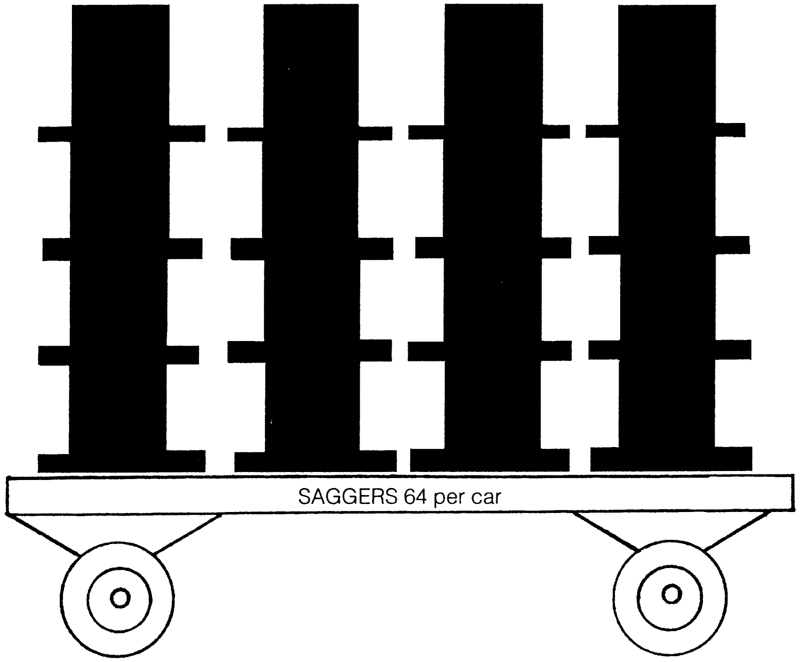


Figure 16.6. Charged, stacked saggers on car ready for oven

pigment. They are valuable. A highly recommended book is *The Physics & Chemistry of Color,* by Kurt Nassau.

Gaseous Reduction of Magnetite

The gaseous reduction of particularly pure magnetite results in a fine, pure, metallic iron powder, $Fe_2O_4 + C \rightarrow 3Fe^\circ + 4CO$. This fine iron powder is used for metallurgical applications, magnets, high-frequency cores, auto parts, catalyst in ammonia synthesis, recording tapes, and many other uses.

Methods

These are the tunnel furnace, the shaft furnace, the static bed, the rotary kiln, the fluidized bed, and the electric furnace.

The tunnel or Höganäs system is probably the simplest method whereby one could get into the production of iron powder on a modest scale, utilizing black sands, and make a significant profit, or as a possible prestep to the recovery of encapsulated precious metals, should they be in of sufficient quantity.

$$Fe_3O_4 + \mathit{Carbon} \rightarrow 3Fe + 4CO \uparrow$$

Looking at this subtitle, we are going to remove the four oxygens from the magnetite, leaving us with three iron atoms. In a large continuous operation, a train of loaded rail cars are slowly moved through a tunnel oven at the appropriate speed.

The tunnel has three distinct zones of temperatures: #1—warm-up zone; #2—reduction zone; #3—cooling zone. The speed of the saggers through the three zones is such that sufficient dwell time is spent in the center or reduction portion of the tunnel with sufficient time for the reduction of the magnetite to go to completion before any sagger moves into the cooling zone. When done this way, it is called a tunnel process.

The product consists of a bushing of sponge iron. The bushing, which is loosely held together, is crushed easily. The crushed bushing is then purified by magnetic separation to recover the pure iron powder.

You can, however, do this on a batch basis and make money.

As for precious values, once you have the reduced magnetite to metallic iron, you can take it up in sulfuric acid, leaving behind values as slimes. Evaporate the filterate to ferrous sulfite, another product.

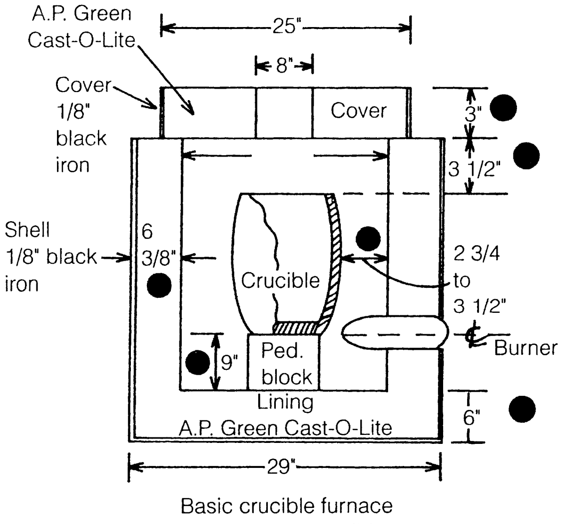
17

Illustrated Melting and Smelting Devices

Some of the Various Devices used Today

Old Standard Lift-Out Crucible Furnace

A much used, simple, gold and silver melter, this furnace is easy to build and operate. It is a fast melter cheap to operate. It can be fired with natural gas, propane, or oil. See Figure 17.1.



Basic crucible furnace
No. 30 to 50 crucible

From this drawing by ratio you can build larger or smaller. The dimensions with the ● remain constant regardless of furnace size, up to a No. 100 crucible.

Blower selection is based on the BTU value of the fuel used.
BTU ÷ 100 = air required.

Normal fuel consumption #30 crucible—oil 2.5 gal per hr.; gas 322 cu feet per hr.; #50 crucible 4.25 gal #2 oil per hr.; 535 cu feet gas per hr.

Figure 17.1. Standard lift-out crucible furnace

Induction (Electric) Furnace

This is an expensive first cost and expensive to operate, very efficient hot melter. Small units can be purchased for melting platinum. The metal charge acts as a short-circuited secondary of a transformer causing the heat for melting. See Figure 17.2.

Cupolette

This small-batch melter uses coke or charcoal fuel. It is great for the recovery of precious metals from buffs and the like. It is also used for the smelting of gold ores or concentrates. See Figure 17.3.

Side-Tap Rotary

This rig is a hot, efficient, smelter and melter. It is good for cons, ore, scrap, and so forth. See Figure 17.4.

Natural Draft Coke-Fired Crucible Smelter or Melter

See Figure 17.5 for the layout of this device.

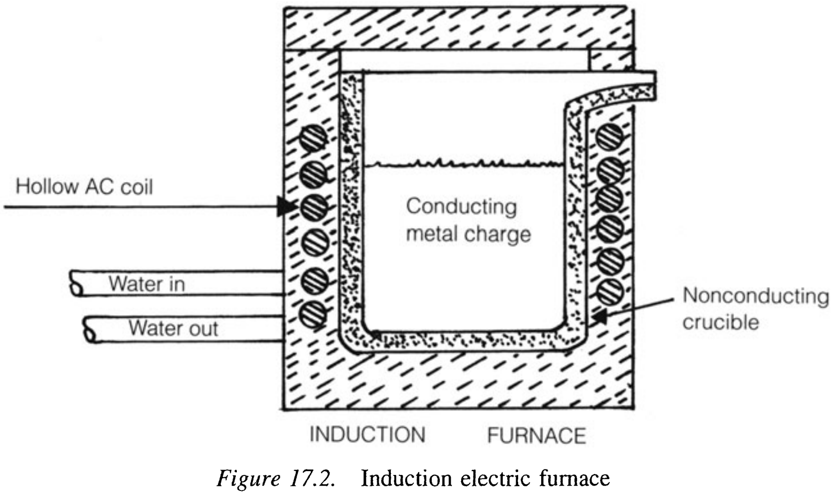


Figure 17.2. Induction electric furnace

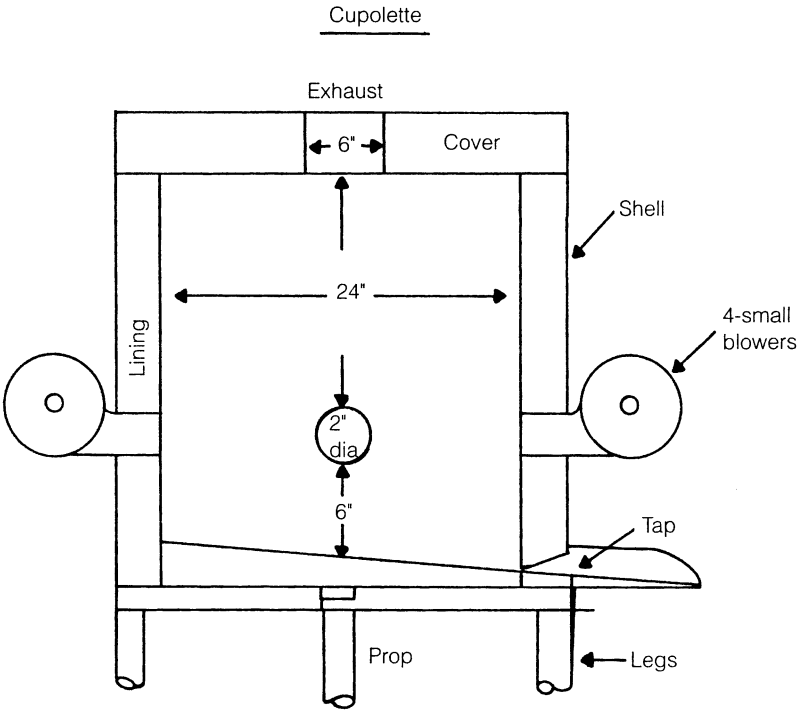


Figure 17.3. Coke-fired batch melter and refiner

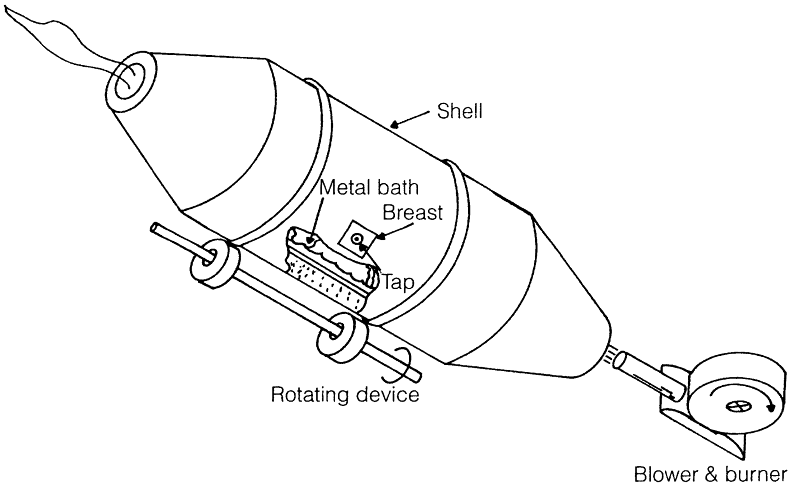


Figure 17.4. Side-tap rotary smelter

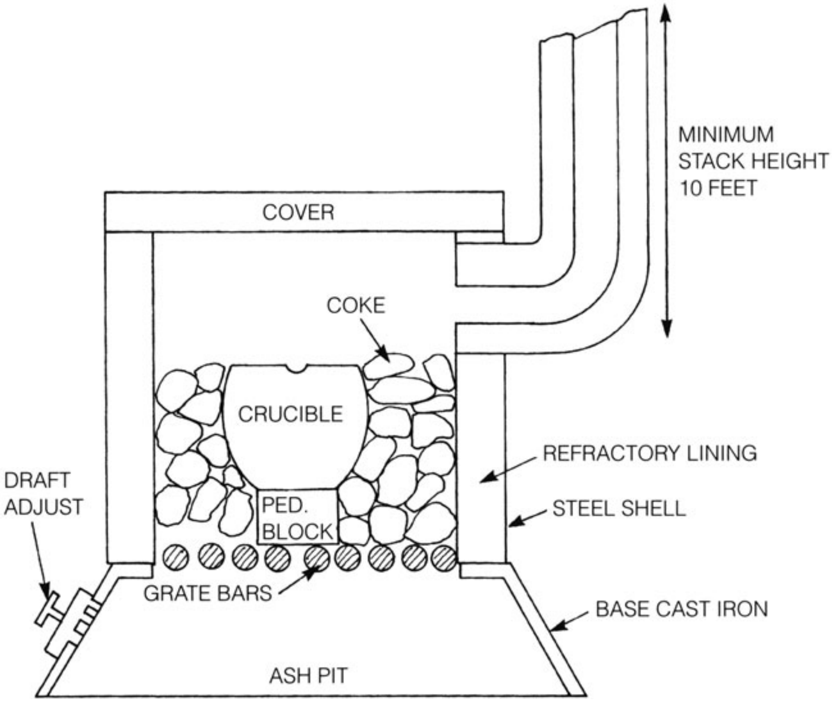


Figure 17.5. Natural draft smelter

Rotate or Rock

Shown in Figure 17.6 is a true rotary on the left and an arc furnace on the right that rocks back and forth to transfer the heat from the lining, adding this heat to the charge and the arc. It is very good melter and an excellent smelter. It is what we used to call a "Detroit Rocker."

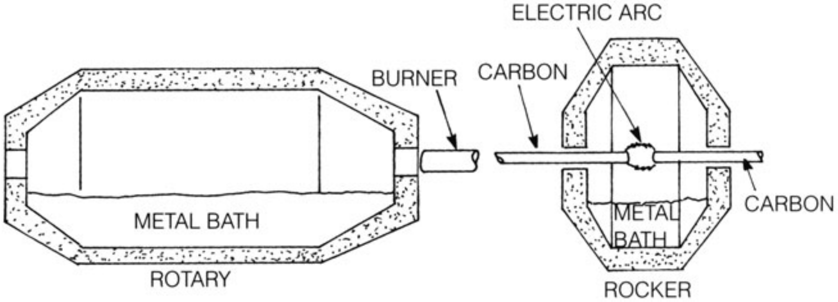


Figure 17.6. Left—true rotary; right—rocker smelter

Burner Design

Two home-brew burner designs for crucible or rotary smelter or melters are presented in Figure 17.7.

Square Brick Crucible Melter and Arc Rocker

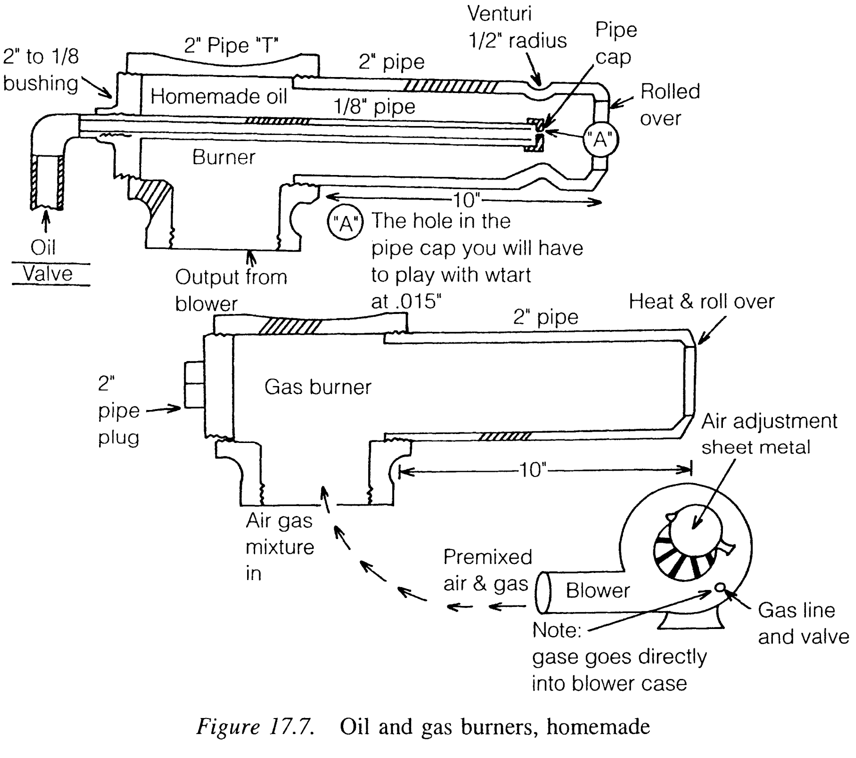
See Figure 17.8 for diagrams of these devices.

Solid-Fuel Crucible Melter

This device is a fired with a hard-coal-bed, coke-fuel natural draft; see Figure 17.9.

Dip Out Crucible and Cast-Iron Melters

These melters are presented in Figure 17.10. On the left is a gas-fired, cast-iron bowl melter, and on the right is a gas-fired crucible melter—both are dip out rigs. Silver can be melted easily in either rig.



"A" The hole in the pipe cap you will have to play with wtart at .015"

Note: gase goes directly into blower case

Figure 17.7. Oil and gas burners, homemade

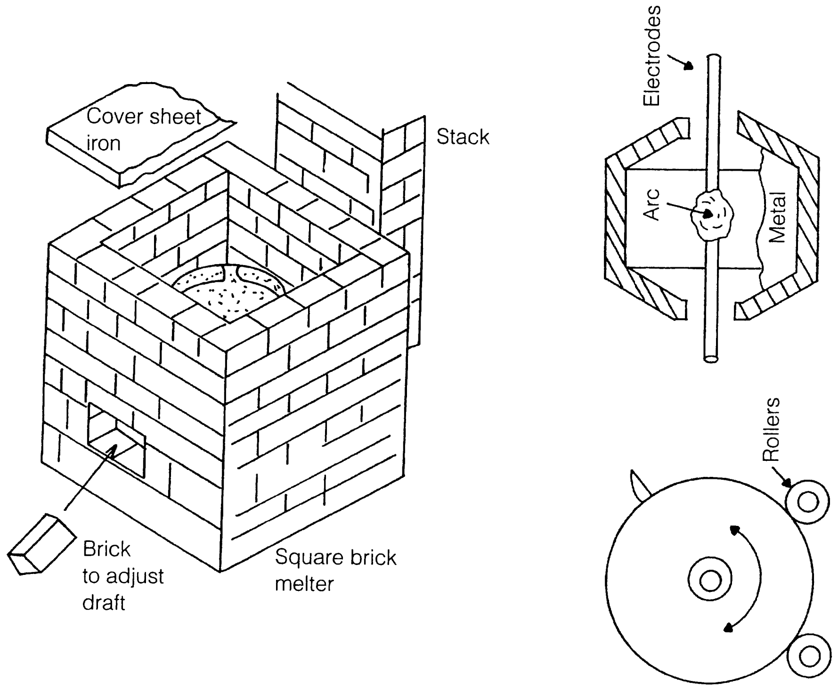
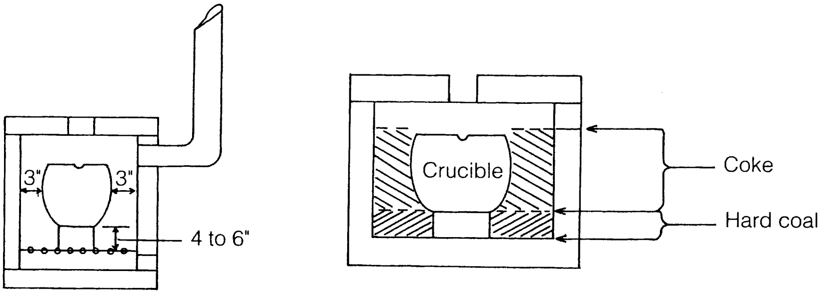


Figure 17.8. Poor man's square furnace and arc rocker



Too much or too little space results in cold melting

Figure 17.9. Solid-fuel-fired melter, natural draft

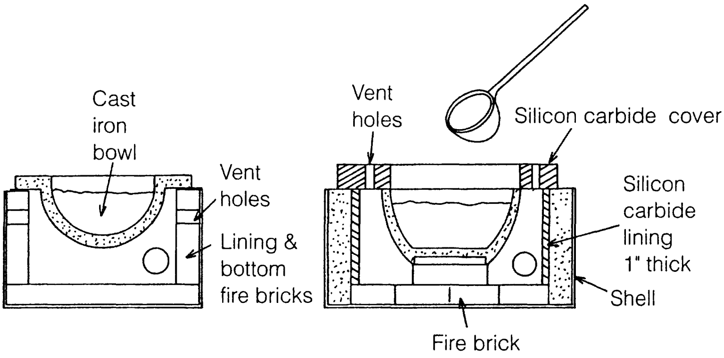


Figure 17.10. Dip out melter, cast-iron pot

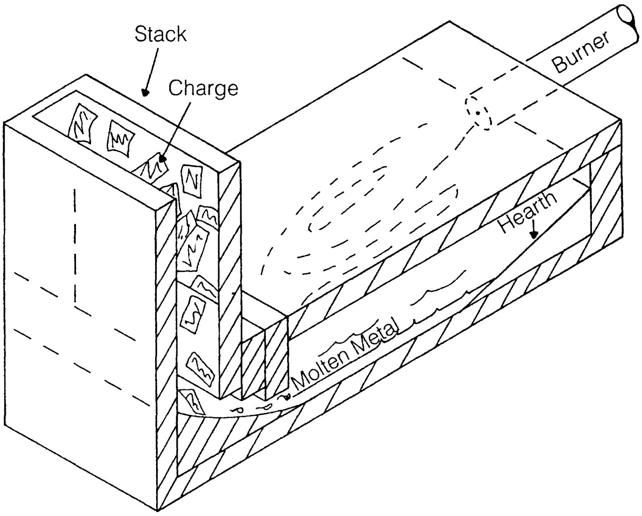


Figure 17.11. Cross section of a reverberatory smelter

Reverberatory Smelter–Melter

See Figure 17.11 for a schematic of a cutaway view of this device.

Dip Out Furnace

In this case, the products of combustion do not come into contact with the metal being melted (oxidizing or reducing); see Figure 17.12.

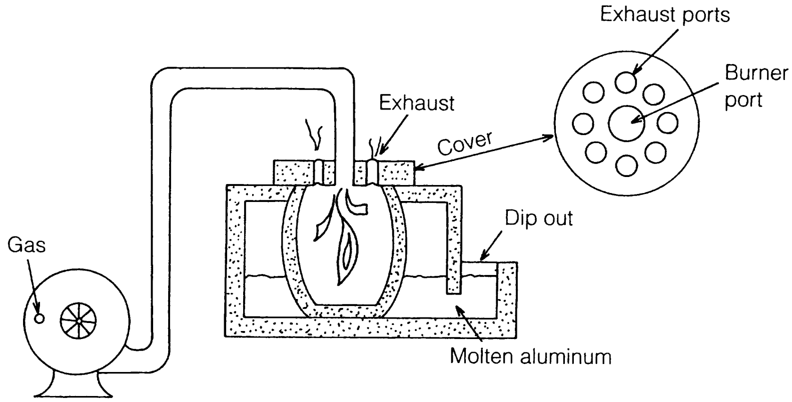


Figure 17.12. Melter designed to isolate combustion products from the melt

Blast Furnace

Cutaway view of a blast furnace used to smelt and reduce ore to metal; the fuel is coke. See Figure 17.13.

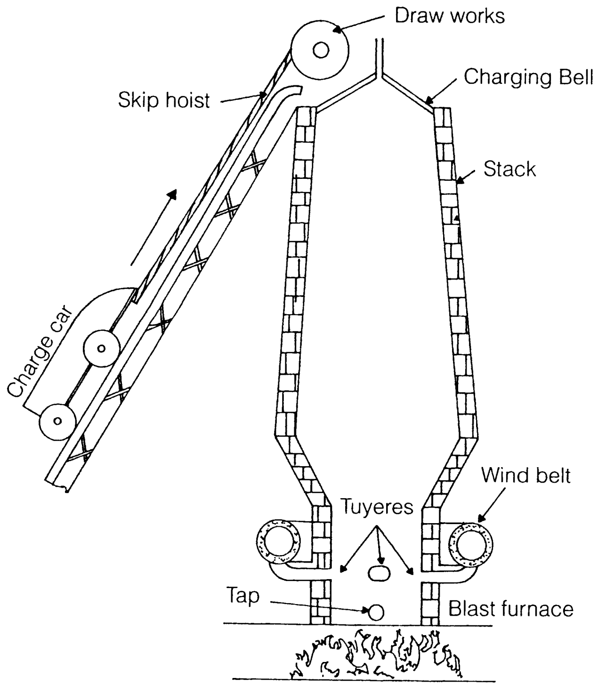


Figure 17.13. Blast furnace to convert metal oxides to metallic metal

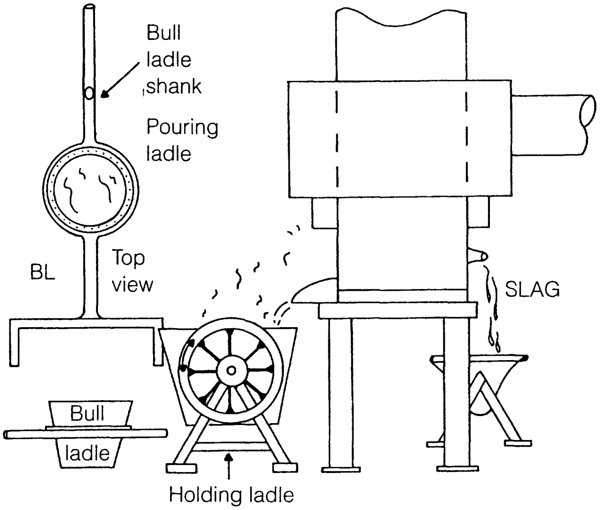


Figure 17.14. Mini blast furnace—melter and smelter

Cupola

The cupola can be used to melt or act as a mini smelting unit. See Figure 17.14. A cutaway view of a standard cupola is presented in Figure 17.15.

Ancient Smelter

These simple but efficient rigs were used to smelt copper and iron ore using charcoal as fuel. Blast air was supplied from water-driven piston air pumps. See Figure 17.16.

Reverberatory Smelter

A cross section of a gas-fired reveraberatory rig is shown in Figure 17.17.

Crucible Rigs

Figure 17.18 presents a natural draft melter (left) and a gas-fired pit furnace (right).

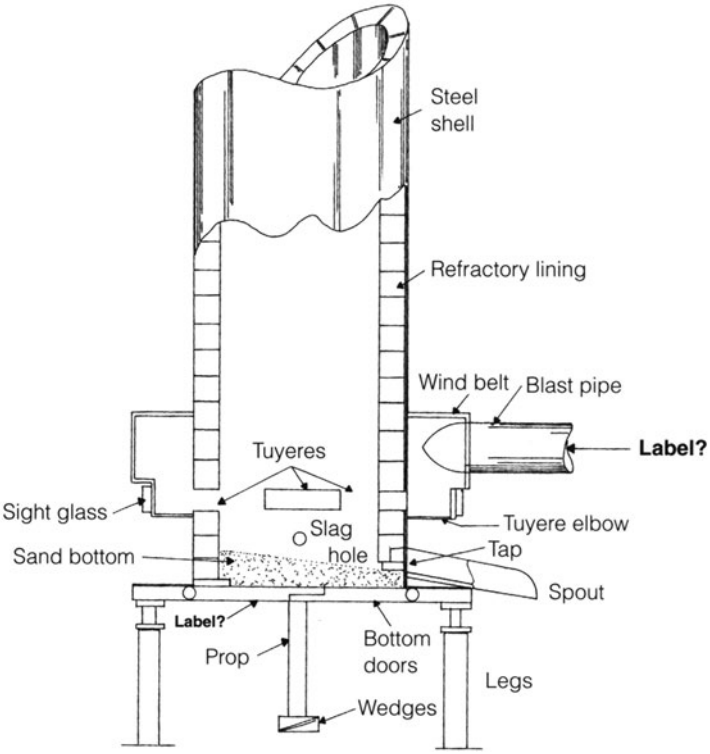


Figure 17.15. Cutaway view of a cupola

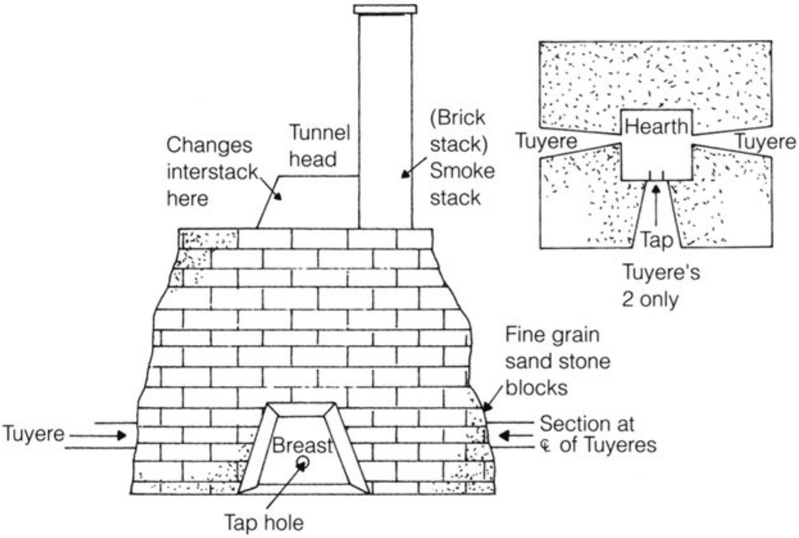


Figure 17.16. Ancient smelter

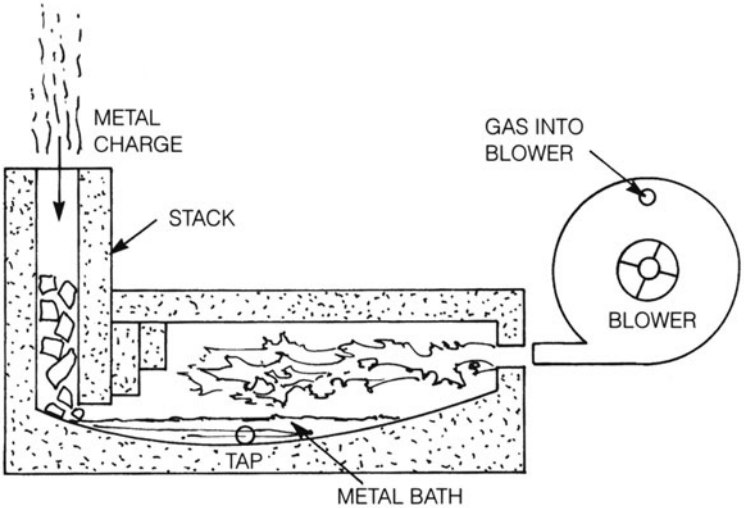


Figure 17.17. Cutaway of a reverberatory smelter

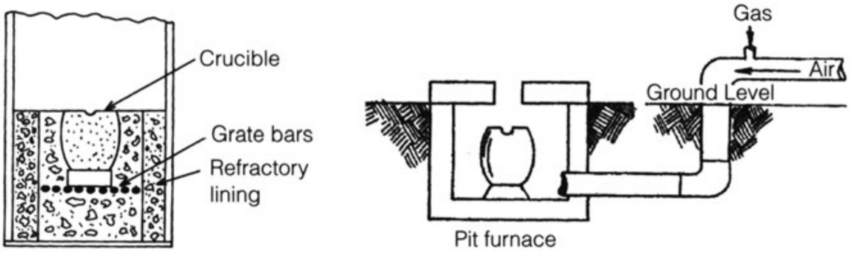


Figure 17.18. Natural draft melter (left) and a gas-fired pit melter (right)

Handled Melting Dish

These are used for melting small amounts of silver, gold, and platinum. See Figure 7.17–19 for a sketch.

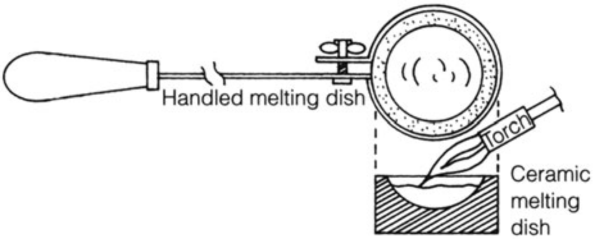


Figure 17.19. Handled melting dish for Pt, Au, and Ag

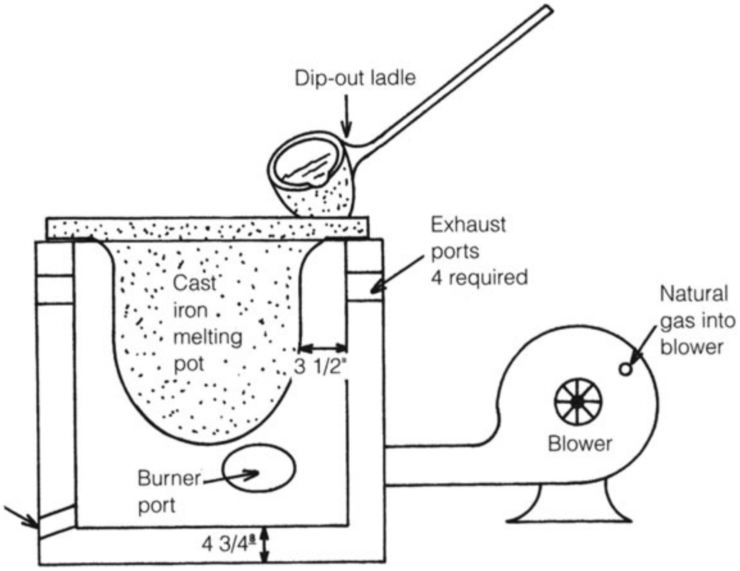


Figure 17.20. Cast-iron pot dip out furnace

Cast-Iron Dip Out Furnace

Figure 17.20 presents another version of this type of furnace.

Tilt-Pour Rotary

The workhorse of rotaries is a great smelting or melting rig. The burner fires through the hole in the charging door. The rotating body is mounted in gimbals, allowing it to be tilted for nose pouring. These furnaces called U.S. Rotary come in five sizes (#1—150 lbs., #2—500 lbs., #3—1000 lbs., #4—2000 lbs., and 4-B—3000 lbs.); the melting capacity inside diameter measures from 13¾ to 33 in. It is either gas or oil fired. I have had the pleasure of using the U.S. Rotary rigs. You have to go some to beat them. See Figure 17.21.

Natural Draft Coke-Fired Dip Out Furnace

See Figure 17.22 for a diagram of this device.

Converted Rivet Forge Furnace

This is a gold and silver melting furnace which is a surprisingly fast melter; see Figure 17.23.

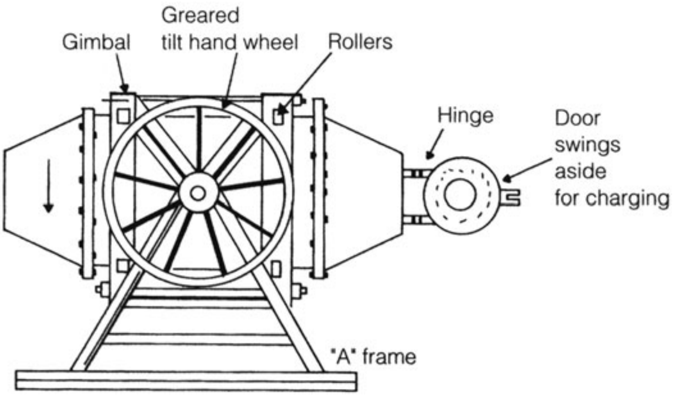


Figure 17.21. Tilt-pouring rotary smelter

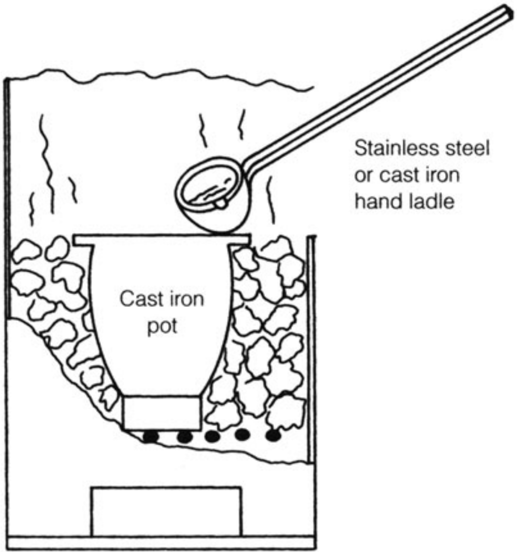


Figure 17.22. Dip out furnace—natural draft

Reverberatory Coke Natural Draft

This reverberatory is coke fired with or without forced draft assistance. It is good for smelting or melting. See Figure 17.24.

Dip Out Reverberatory Smelter

See Figure 17.25 for a sketch of this device.

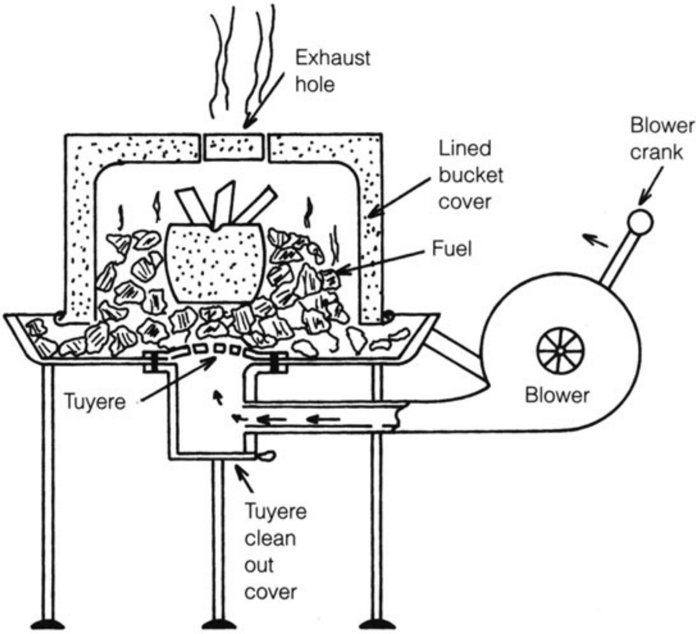


Figure 17.23. Melter made from an old rivet forge

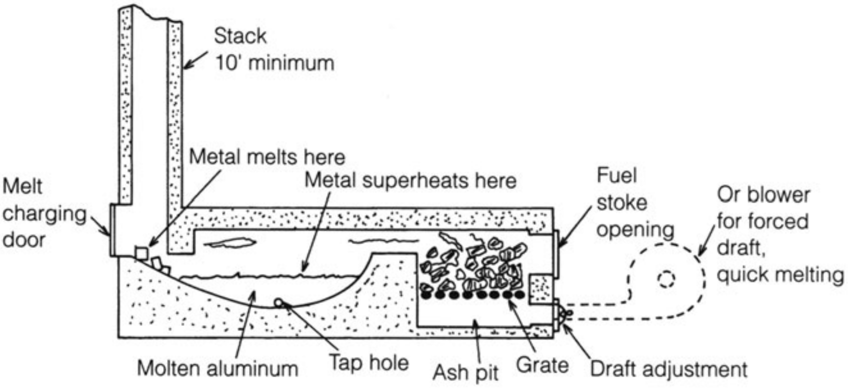


Figure 17.24. Solid-fuel reverberatory smelter

Tilting Cast-Iron Pot Furnace and Pot Design

Figure 17.26 presents a diagram of this device.

Bull Ladle Melting Furnace

Two views of this device is presented in Figure 17.27.

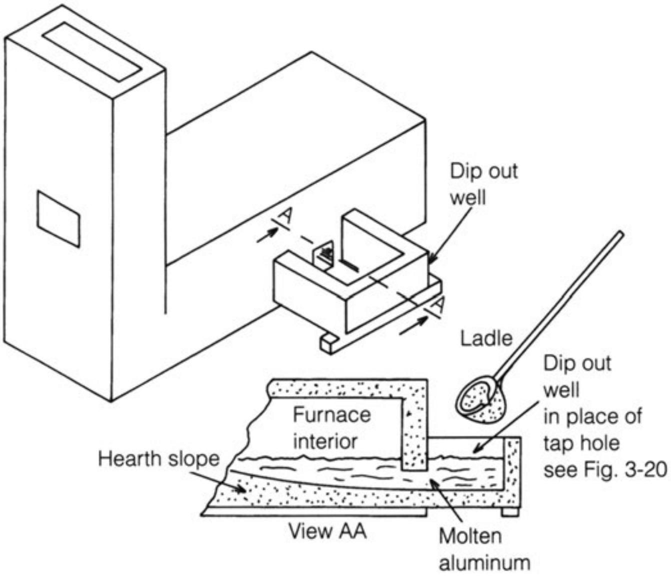


Figure 17.25. Dip out reverberatory melter

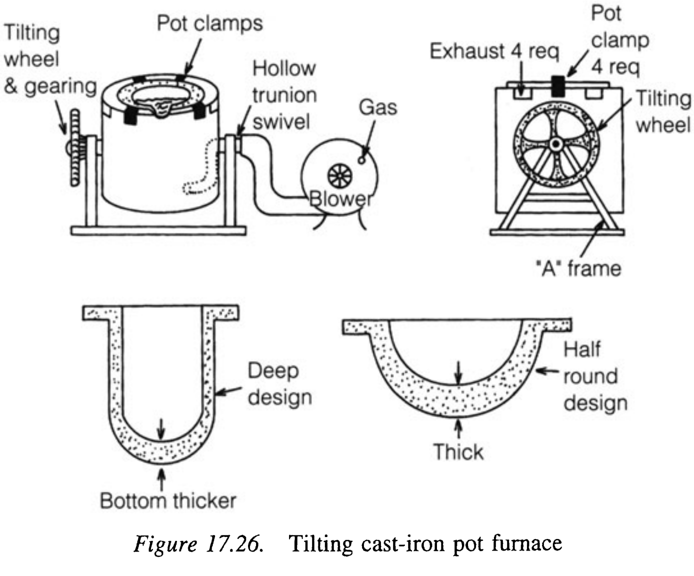


Figure 17.26. Tilting cast-iron pot furnace

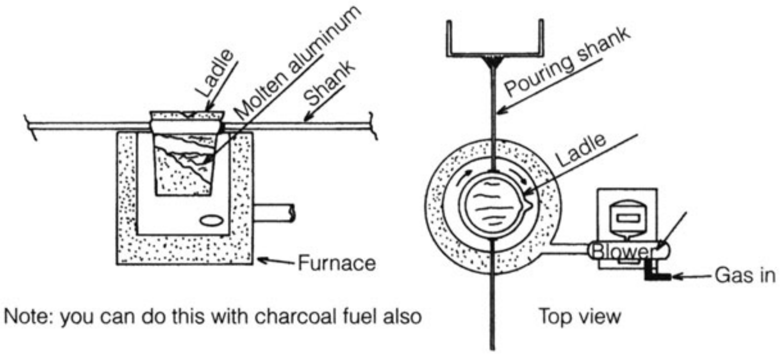


Figure 17.27. Two views of a bull ladle furnace

Natural Draft Melter with Cast-Iron Cover

See Figure 17.28 for a schematic of this melter.

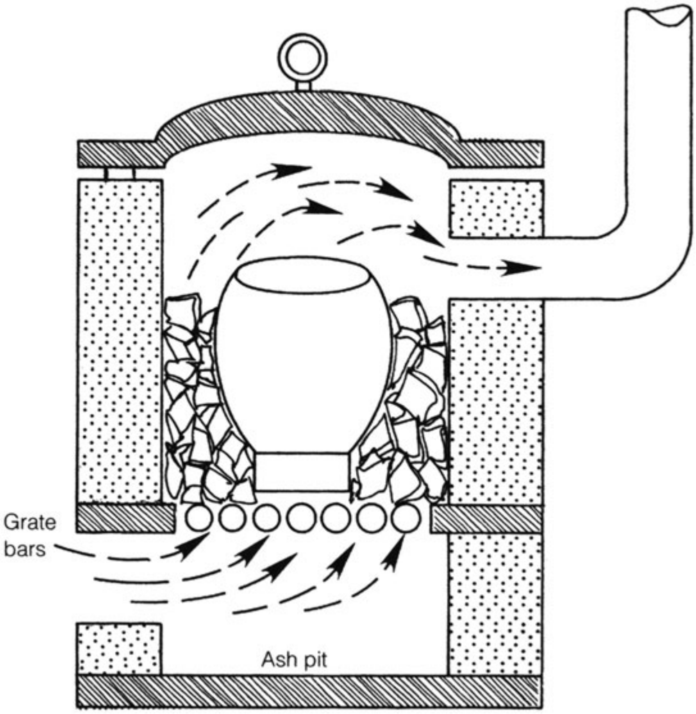


Figure 17.28. Natural draft melter with cover

Direct Arc and Indirect Arc

In the direct arc, the arcing is between the metal and the electrodes, not between the electrodes. In the indirect arc, the arcing is between the electrodes, and not the metal. See Figure 17.29.

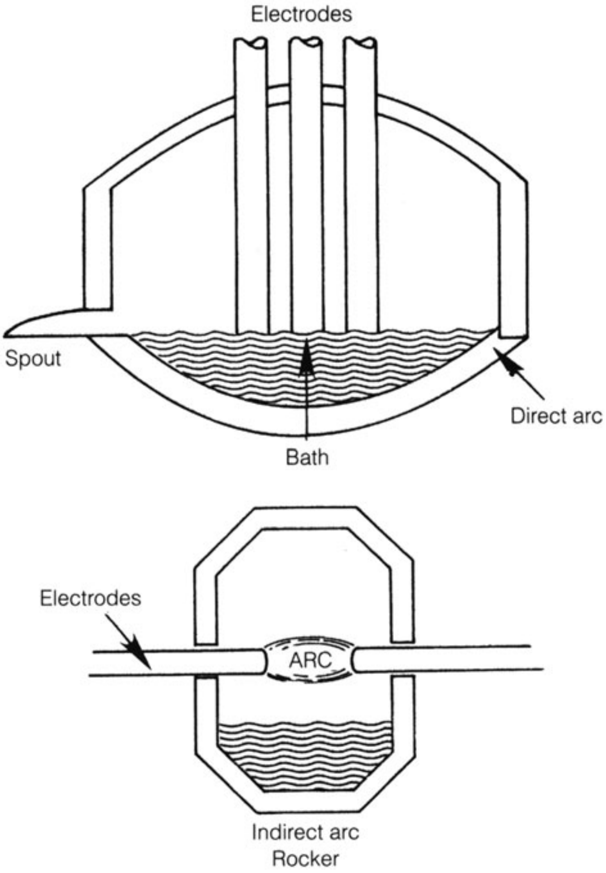


Figure 17.29. Direct and indirect arc melters

Fore Hearth

A Fore hearth is attached to the front of any melting device as a receiver in order to collect a large amount of metal when needed. See Figure 17.30.

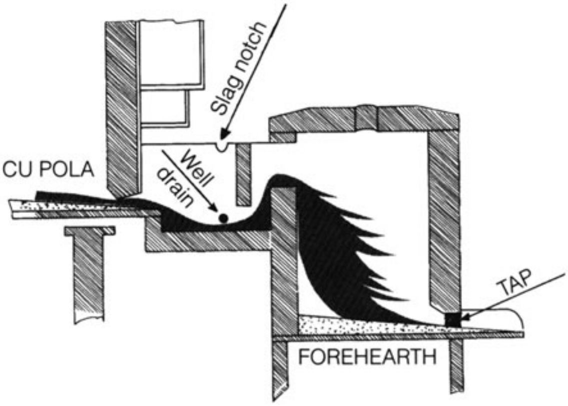


Figure 17.30. Fore hearth

18

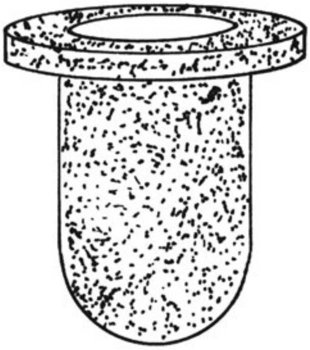
Odds, Ends, and Author's Do's and Don'ts

Activated Charcoal

Activated charcoal is one of the most amazing and useful substances in the world, and it is the most useful adsorption agent. The most active charcoal is produced from willow or other similar woods, pyrolized at a low heat not to exceed 550°F over a long period of time so that the reactive volatiles (that is, hydrogen and oxygen) are not driven off. A 1-ounce sample has an aggregate total surface area of roughly 13 acres. It has hundreds of uses, some dating back many centuries—fuel, fireworks, gunpowder, medicinal healing, gas masks, deodorizing gasses and liquids, decolorizing, precious metal recovery, and so forth.

Cast-Iron Crucibles

Cast iron can be used to melt silver, lead, and aluminum. Melting bowls to do this come in a wide variety of sizes. See Figure 18.1.



CAST IRON

Figure 18.1. Cast-iron melting bowls

The bottoms are cast thicker than the sides for longevity of the bowl. The bowl is coated with a colloidal solution of graphite in water and then dried to prevent melt contamination. The melting points of the metals melted in the crucibles are as follows:

Ag = 961°C (1761.8°F); Pb = 327°C (620.6°F); Al = 660°C (1220°F).

Cupel Capacity to Absorb Lead

The following list presents the capacity of a cupel to absorb lead:

¾-in. cupel—3 g
⅞-in. cupel—5 g
1-in. cupel—8 g
1⅛-in. cupel—10 g
1¼-in. cupel—16 g
1⅜-in. cupel—20 g
1½-in. cupel—28 g
1⅝-in. cupel—40 g

Masking is Necessary

When you have a solution which has in its makeup ions which will interfere with the results of your analysis, there are numerous reagents one can use to mask the troublesome ions to prevent interference. Iron ions are often problem ions and can hide the presence of some PMG ions. There are also reagents used to demask what you have previously masked, thus bringing you full circle.

Adjusting Furnace to Fire Reducing or Oxidizing

Regardless of whether the furnace is fired with natural gas, propane, or oil, if you adjust the burner fuel to air input (mixture) to the point where the combustion noise is loudest, you are firing, neither reducing nor oxidizing but neutral. If, at this point, you reduce the air input to your burner by a little, you have moved into a reducing mode. Increase the air and you move into the oxidizing mode. If you hold a piece of bright zinc into the furnace exhaust for a few seconds and it remains bright when removed, you are firing on the reducing side. If the bright zinc test strip turns gray-white quickly (zinc oxide coating), you are oxidizing. Some use a cheap decibel meter and do it all by sound.

Do not reduce ammonium chloroplatinate salts by mixing the damp salts with zinc dust. The product will be of poor quality.

Do not use H_2SO_4 as a dessicant; use calcium sulfate (Drie Rite). H_2SO_4 reacts with olefins and basic compounds.

Under no conditions get involved in any precious metal recovery process, mechanical or chemical, that deviates from logical principles or classical chemistry.

There are plenty gold snake oil scams out there, some even touting patented equipment and processes. The patent office requires no proof that a process, mechanical or chemical, actually does what the patent claims. It stands to reason that if someone comes up with the panacea, they will simply set up and make themselves rich, not offer it to you (at a price) so you can get rich. That is the law of greed.

The warning words in a scam promo are scenario, extrapolate, new discovery, Hi tech, and so on. See or hear any of these, and it is time to run.

Chimney Data for Natural Draft Smelting, Roasting, and Melting Devices

The general use for a chimney is first to provide draft and thereby produce the combustion of a fuel, and second, to carry away the products of combustion. The first requirement, the draft, is governed by the height, and the second requirement is governed by the inside diameter of the chimney. Thus, the taller the chimney, the more draft it will produce [that is, combustion (horsepower)]. The draft is the difference in pressure produced by the difference in weight between the hot gasses inside the chimney and the equivalent column of outside air. The intensity of the draft is measured in inches of water and determined theoretically by the following formula:

$$D = 0.518\ P_o H \left(\frac{1}{T_o} - \frac{1}{T_e}\right)$$

where D is the draft in inches of water, H is the height of the chimney, P_o is the observed atmospheric pressure in pounds square inch, T_o is the absolute outside temperature in degrees Fahrenheit, and T_e is the absolute temperature of the chimney gasses in degrees Fahrenheit.

One inch of water equals 0.58 ounces per square inch. Some 100-ft chimney ratings in horsepower (HP) follow:

100-ft tall, 6¼-ft inside diameter = 1000 HP

100-ft tall, 3½-ft inside diameter = 250 HP

100-ft tall, 4½-ft inside diameter = 500 HP

One inch of mercury = 13.596 in. of water.

Planetary Symbols for Metals

Sun = Gold
Moon = Silver
Venus = Copper
Mars = Iron
Mercury = Mercury
Jupiter = Tin
Saturn = Lead

Old but Useful Method to Purify Off Specification Gold

In this method, the gold is melted with antimony sulphide. The antimony sulphide reacts with the base metals, producing sulphides of base metals and free antimony. These sulphides are skimmed off and the resulting gold antimony metal alloy is then heated to a temperature above 1635°C (2975°F) to vaporize off the antimony, leaving pure gold. There is a spread of 2111°F between the vaporizing point of antimony and gold which makes this a viable method.

Specific Gravity of Solids

W = weight of substance in air

w = weight of substance in freshly boiled distilled water

$$\frac{W}{W - w} = \text{SG.}$$

See Figure 18.2. The specific gravity (SG) of some metals are as follows:

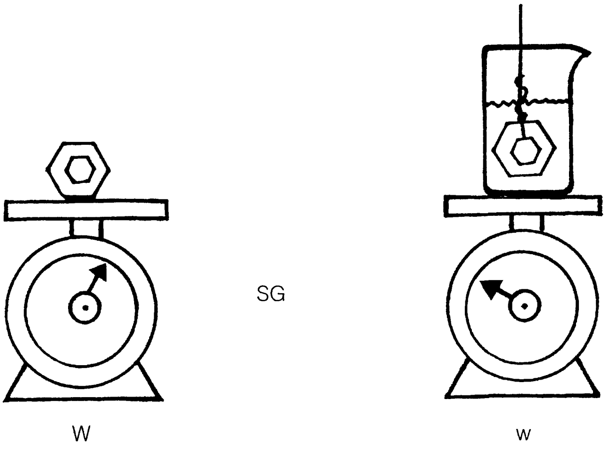


Figure 18.2. Taking the specific gravity of solids

Gold—19.3
Platinum—21.45
Silver—10.53
Palladium—12.0
Lead—11.35

Preparation of Proof Gold and Proof Silver

Proof Gold

Dissolve practically pure gold (cornets) in aqua regia (nitrohydrochloric acid) and dilute by two volumes of distilled water. Let this stand very still for 5 days to allow any silver chlorides to settle out. Decant the gold chloride solution very carefully by siphoning. The gold chloride solution is then evaporated almost to dryness (a thick syrup). Add plenty of distilled water to take up the syrup. To this, add a few cubic centimeters of sodium bromide solution. Allow this to stand for 5 days. Decant this solution by siphoning. Place a few pieces of chemically pure aluminum foil in a beaker. Now add your siphoned gold chloride to the beaker containing the chemically pure aluminum foil, dropwise with a burette. When precipitation is complete, add enough hydrochloric acid to dissolve excess chemically pure aluminum. The residual gold is washed thoroughly with distilled water by decantation. The gold is then dried. Place the dried precipitated gold in a new, clean cupel. Cupel the gold into a bead; roll the bead into a thin strip for use. (Do not cupel with lead.)

Silver Proof

Dissolve some chemically pure silver foil in nitric acid, and then filter off the solution. Precipitate the silver as a silver chloride with hydrochloric acid. Filter off the chloride and wash several times on the filter with diluted hydrochloric acid. Place the silver chloride in a beaker of dilute hydrochloric acid and add some chemically pure aluminum foil. The aluminum foil will reduce the silver chloride to metallic silver. Wash the silver and dry. Place the dried silver in a clean, fresh cupel and melt into a bead, then roll the bead into a thin strip for use. You can make up Pt and Pd proofs as you did for the gold proof or work the chloride salts of Pt into purity and Pd chlorate into purity, then reduce with chemically pure aluminum.

By making up proofs and putting a known weight of a proof into a known volume, you can use these in your thin-layer chromatographic work to establish R_f values and so forth.

Iron Collector for Precious Metal Assaying

This method has a great deal of merit when you consider the affinity of iron for precious metals. The method is quite simple. The finely ground sample is mixed

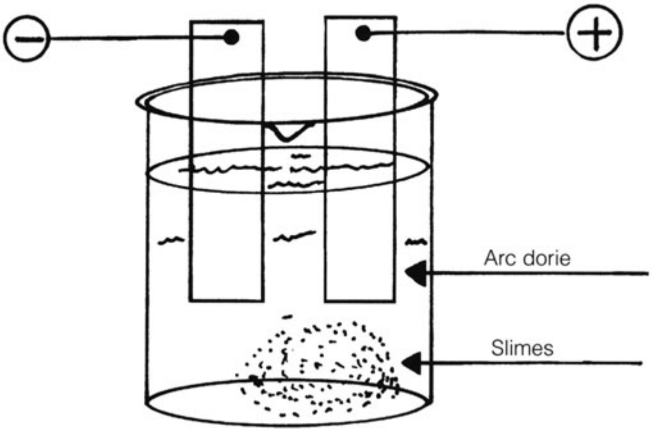


Figure 18.3. Iron as a collector for precious metals

with a little flux (borax) and pure iron (collector). This is melted using a DC carbon arc to produce an iron precious metal doré anode. The anode is placed in a beaker and the Fe electroplated off onto an iron cathode, using Fe fluoborate as an electrolyte. See Figure 18.3. The resulting slimes are now collected, washed, dried, and fire assayed as follows:

5 g of dried anode slimes	40 g of PbO
5 g of wheat flour	40 g of borax glass
40 g of SOD. carbonate	3 g of barren silica
Fuse at 1000°C	cupel a Pb button

Recovery of Platinum Metal Group from Auto Catalytic Converters

One method is similar to using Fe as an assay collector. It is reported that the catalytic converter rods, honey comb, and pellets (Al_2O_3 + PtPd Rh) are simply smelted with scrap steel in an electric arc furnace; the molten steel precious metal alloy teemed into H_2O to granulate it. The granulated metal is then digested in a 20% by volume of sulphuric acid. The values are now concentrated in the insolubles. See Figure 18.4.

Another method is via gas phase, also known as gas-phase transport. In this method, the values are converted into volatile chlorides (gas) of PtCl, PdCl, and so forth. These chlorides are then collected by a condenser or trapped on NaCl crystals. The material is heated and a gas-phase composition is passed through the heated material where it converts the metallics to their respective volitale chlorides which exit the reactor as a gas phase to be captured on salt or condensed. See Figure 18.5.

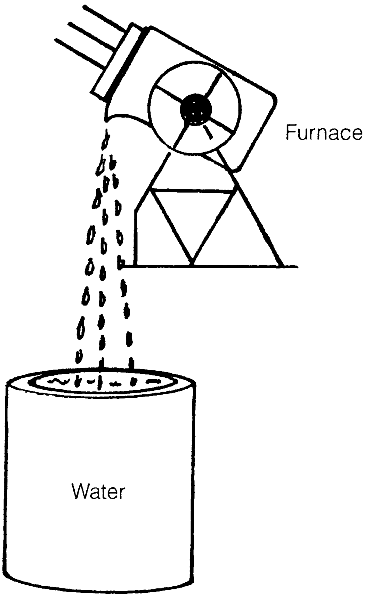
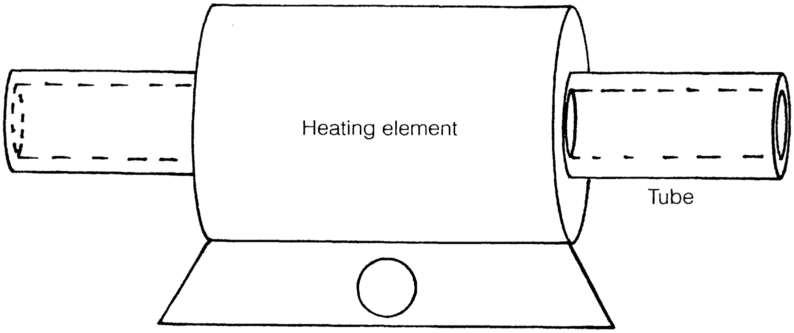


Figure 18.4. Values remain behind as insolubles

For the catalyst Al_2O_3 + Pt and Pd, the values can be removed from the substrate as a gas phase (transport) with the following gas-phase compositions:

50% Cl_2 5% CO 45% Ar	50% Cl_2 50% Ar	95% Cl_2 5% CO_2
9% CCl_4 91% Air	95% Cl_2 5% CO	20% $COCl_2$ 80% CO_2



Combustion tube furnace

Figure 18.5. Values captured as chlorides on salt

The reaction temperature range is 800–900°C; the flow rate is from 5 to 12 L/h. The low end of recovery is 94% and the high end of recovery is 99%.

PGM can be chlorinated in a stream of dry Cl_2 or any of the 6 chlorinator mixes above. If mixed with a tenfold excess of NaCl in a boat at 600°–700°C, the Rh, Pd, Ir, and Au remain in the boat. At 800–900°C, they gas phase transport. The Os and Ru gas phase easily and early at relatively low temperatures and should be absorbed in several traps with 6 *M* HCl saturated with SO_2.

Some Stable Halides

NaCl, CuCl, AgCl, AuCl, $MgCl_2$, $CaCl_2$, $PbCl_2$, $NiCl_2$.

Aqua Regia

3 HCl + 1 $HNO_3 \rightarrow NOCl + Cl_2 + 2H_2O$. Leffort or Lunge is 3 parts HNO_3 + 1 part HCl (a backward aqua regia).

Ammonium Iodide

Decomposition with ammonium iodide is statu nascendi (produced in position). Some iodides are decomposed by heating in air to yield the oxide and free iodine (that is, stannous plus heat → iodide plus tin oxide). Ammonium iodide at ~ 200°WC yields HN_3 + HI.

Van Arkel and Boer Process

Here again, we have a vapor transport system. This system is used mainly to purify (refine) an impure metal:

$$M + 2I \xrightarrow{400°C} MI.$$

On the left side of the reaction, we have M, the impure metal, + 2 iodine. When heated to 400°C, we wind up with M as a pure metal iodide. If we raise the temperature of MI from 1200°C to 1300°C, we wind up with M + I (pure metal and iodine). The iodine is reused. This method is limited to metals of a high valence (that is, titanium, zirconium, hafnium, and thorium),

Le Platime du Monde (Platinum of the World)

M. Louis Duparc came up with a rather simple method of refining and separating the PMG from raw platinum recovered from placer operations.

1. Dissolution in aqua regia of Pt, Pd, and Au in solution, and Os, Ir, gangue, and so forth as insolubles.
2. Precipitation of the Pt from solution as ammonium chloroplatinate; calcination to Pt sponge.
3. Separation of iridium as ammonium chloroiridate on long standing. NOTE: When you drop Pt as ammonium chloroplatinate from a mixed bag PMG with ammonium chloride, the iridium precipitation is a delayed action. Leave it stand and in time it will come down, sometimes overnight. The ammonium chloroiridate can then be calcined to Ir sponge.
4. At this point, iron or zinc is added to the mother liquor, which will bring down what is called, by M. DuParc, first blacks. Dry and roast these blacks and scrub with dilute sulphuric acid. This removes any base metals which may be present. At this point, you have in the metallic state other metals of the PMG.
5. The scrubbed first blacks are now digested in aqua regia to take up the palladium, leaving any rhodium in the residue (insolubles).
6. This solution is now treated with ammonium chloride to remove any traces of Pt, Rh, and Ir. The solution is stripped of its palladium with metallic iron, calcined, and sold as palladium sponge.
7. The insolubles from Step 5 are fused with barium dioxide, potassium pyrosulphate, or sodium peroxide. The fusion is digested with aqua regia, de-noxed, and the Ir and Rh are recovered as ammoniun salts with ammonium chloride and calcined to sponge.
8. The insolubles from our first aqua regia digestion (Os–Ir, etc.) are fused with zinc. This zinc Os–Ir alloy is digested in aqua regia. This acid liquor is steam distilled to remove the Os as osmic acid trapped in gas washing bottles. It can be converted to metal; however, it is usually sold as osmic acid.
9. The acid liquor from which we distilled off the Os as osmic acid is then rid of the iridium and rutenium, again with ammonium chloride as their respective salts. Calcine to sponge. Other than SX (liquid/liquid separation), there has been little change in the method of separating and refining the PMG.

Depletion Plating

It was a common practice in ancient times for goldsmiths to defraud, in some cases, and in others to enhance an object of art or jewelry by electroplating or the applying 24kt gold leaf to an object. The Incas were very good at it, so much so that it got them into lots of trouble with the Spaniards who looted their gold artifacts and religious icons.

Many of the gold objects produced by the Incas (casting and fabrication) were not pure 24kt but off-spec gold (that is, 12kt, 14kt, etc.). What the Incas did was to pack these off-spec items in a mixture of approximately ⅓ NaCl, ⅓ NH_4Cl, and ⅓ brick or pottery dust by volume. In pots (crucibles), a cover was luted in place. The pot was then heated to a point just below the melting temperature of gold.

For several hours, the NH_4Cl and NaCl will leach the base metals from the surface as chlorides (that is NiCl, CuCl, AgCl, etc.). These liquid chlorides are absorbed by the brick dust. This leaves the objects surface covered with a porous surface of considerable depth of pure gold. This surface of pure gold is then burnished smooth, giving the item the appearance of a solid gold object. When the Spaniards got their ill-gotten loot home and did a little specific gravity checking, they found that many items they thought were solid gold were indeed not. Thinking that the Incas were intentionally deceiving them, upon their return they killed many of them.

I have seen a lot of counterfeit gold nuggets produced by depletion plating. As to a more correct treatment temperature due to the fact that when you melt copper and gold together 14kt gold = 14/24 gold and 10/24 copper. You now have an eutectic mixture whereby the gold will melt at below its melting point. You must consider this. I have found that the depletion plating from 14kt to 6kt works fine if you hold the temperature of the mix and object to a nice red, red heat. Pure gold melts at 1945.4°F, so at 1200°F, you are in good shape.

Garth Muran Popsicle Assay Method

This method is simple, quick, and highly effective. It also has a broad range as far as types of ores, black sands, and so forth on which you can use it.

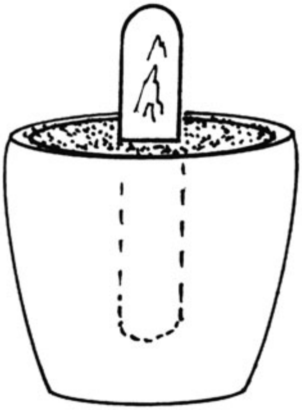
The sample to be assayed is wrapped in lead assay foil. The assay crucible is filled with borax glass to one-third its capacity. The lead-wrapped sample is placed in the middle, then covered to within ½ in. of the top with borax glass. The center of all this is wet down with silver nitrate solution, and a popsicle stick is punched down through the center. See Figure 18.6.

The assay is fused at 1000°C for 1 hr. The lead prill is poured off and cupelled.

Decomposition

Once you have a material that has been milled, concentrate it to the desired point. You must now decompose it in some fashion in order to separate the values from the gangue. If you are refining scrap secondary material such as jewelry and the like, where the precious metal content is very high per unit of weight, your choice for a solvent could very well be aqua regia, even at its high cost.

You have dozens of solvents from which to choose: various acids, mixes of



Popsicle assay

Figure 18.6. Popsicle stick assay

acids, bromides, cyanide, and so on. In the last few decades, the solvent of choice in many small and large operations has become hydrochloric acid and Cl_2 (gas) due to its relatively low cost and efficiency of putting values into solution. The material is placed in a glass-lined reactor and sparged with Cl_2. The excess Cl_2 is scrubbed and recycled. A typical scenario would look like this. Use raw material ore concentrates, electronic scrap, and so forth, containing PMG, Au, Ag, and base metals. Digest in the reactor with HCl/Cl_2 at 208.4°F.

The insolubles Rh, Ru, Os, Ir, Ag, Pb, and so on are leached with HNO_3 to remove Ag and Pb, which is leached with HCl/Cl_2 at 208.4°, leaving the Ag as an insoluble chloride. The solution is neutralized with NaOH: at this point sodium bromate ($NaBrO_3$) is added and the Ru and Os are distilled off and absorbed in a weak HCl solution. The mother liquor is now neutralized with NaOH to drop out the base metals as solid hydroxides, which are filtered off. The mother liquor is a 3 or 4 M concentration with HCl. The Au is removed by SX with dibutyl carbitol, Pd with di-*N*-octylsulfide, and so forth. It is common practice to more or less work out a process that works best for you and the material at hand. The key is that you must follow the rules of chemical systems—classical chemistry.

Bacterial Preoxidation

Although bioleaching and biobenefication systems have been around for quite some time, the jury, as far as I can see, is still out, and will be out for some time to come. Should one wish to look into this, there is a mountain of data available.

Some of these data are highly suspect and lots of conflicting theory and conflicting results. The basic idea behind all this is to have various bacteria (bugs) (that is, ferro-oxidants) oxidize the cons, flotation products, or slimes.

This preoxidation treatment is supposed to condition and render the material more amenable to the leach of your choice, be it cyanide, an acid, or mixed acids. After wading through a mountain of some of the studies, I would approach the whole thing, at least for now, with a jaundiced eye.

Bench tests by myself have shown no gain in recovery, only a gain in cost. Here we go again with man's tendency to complicate things that were simple and working. When you crunch the numbers, it does not come out too well. If you recover, say, 98% of the value for *X* dollars and jump this up to 99% recovery (with a costly complicated system) for 100*X* dollars, you are the loser. At present, there are some very large outfits spending millions of dollars chasing the bugs, good luck.

Go back in history and study what went on long before we showed up. It is an eye opener.

Appendix A

Assay of Black Sands[1]

By Paul Hopkins[2]

The following methods have been selected from a large number tried while assaying several hundred samples of placer concentrates. It is thought that some of these methods may be useful to those who are required to assay similar products containing large quantities of metallic particles, such as jeweler's sweepings.

No great difficulties will be encountered in assaying black sand from beaches or river bars. Such samples require care in grinding and sifting so that no oversize particles of gold or platinum are lost. It is also necessary to have sufficient silica in the flux to form a fluid slag with the excess of iron, magnesium or chromium which such samples contain.

It is much more difficult to assay black sands, or concentrates, produced in large-scale placer-mining operations. These products are usually much harder and more abrasive than the beach black sands. They also contain numerous metallic particles resulting mainly from wear on the mining machinery. These particles consist chiefly of iron or steel but also contain lead, copper and alloys such as babbitt, solder, brass, ferrosilicon, etc. Fairly large particles of gold are often found. Some samples will contain as much as ten percent of such metallic particles. It is not feasible to remove the particles of iron with a magnet and discard them, as they invariably contain gold, sometimes a considerable amount. This gold is attached to the iron particles by rust or wedged into cavities. Scraps of sheet iron are often found which have become tightly folded or rolled and contain gold or amalgam within the folds.

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[1] *Reprinted from* U.S. Bureau of Mines Report of Investigations 3265.

[2] *Associate analytical chemist, U.S. Bureau of Mines.*

With a sample containing large metallic particles it is often advisable to grind by stages, sifting the sand through successively finer screens and setting the grinder a trifle closer after each screen. The metallics removed on each screen are retained. It is very difficult to grind some black sands finer than 30 to 40 mesh with a disk grinder. When this size is reached, the sand grains merely cut grooves in the disks and are not reduced further. In such cases it is necessary to finish the grinding on a bucking board or in a ball mill.

If a sample is extremely difficult to grind it may be ground to 30 to 40 mesh and a large quantity taken for assay, such as 500 to 1,000 grams. This sample may be fused in a graphite crucible with soda, borax glass and 50 to 100 grams of lead. Enough sulphur should be present to form a sulphide with all of the metallic iron present. The sample may contain sufficient pyrite or other sulphide for this purpose, or sulphur may be added as such or in the form of galena. If the sample contains a large quantity of sulphides, litharge should be used in place of metallic lead. After complete fusion, the melt is poured into a large conical mold. The lead button may then by scorified and cupelled and the slag weighed, ground and assayed. If a layer of matte has been formed, it should be ground with the slag. This method consumes much time and material but is recommended for high-grade samples.

It is possible greatly to reduce the labor of grinding by removing the metallics at two or three selected screen sizes and cutting down the amount of sample at each lower size. This is illustrated in an example given later.

Many methods for assaying the metallics were tried. An acid treatment similar to that used for gold in copper bullion is feasible but consumes much time. It is possible to oxidize the particles in a covered crucible by using oxygen at red heat. This method was found to consume too much oxygen to be practical. Scorification is not practical on the larger size particles as the slag closes over them before they are oxidized. The most satisfactory method is the use of sulphur or a sulphide.

Outline of Method

Weight entire sample, crush if necessary, and screen through 4 mesh. If metallics are found larger than 4 mesh, remove, weigh and retain them. Add to the screened sample an amount of crushed barren quartz equal to the weight of the metallics removed. This will simplify the final computations. Reduce the amount of sample by quartering or riffling to a weight depending on the probable grade. Two pounds may be sufficient for a low-grade sand, but as much as 20 pounds may be necessary for a high-grade sand. Weight the split sample and feed it slowly into a disk grinder set to produce an 8 mesh product. If the grinder stalls, as will often happen, open it and allow the contents to drop into pan after first removing the product already ground. The particle which stalled the grinder may now be picked out and the remainder fed back. Sift on 8 or 10 mesh screen. If the oversize still contains unground sand particles, pick out the larger steel fragments, retain them, and feed the oversize back into the grinder after setting it somewhat closer.

The sample is put through 14 and 20 mesh screens in a similar manner. On some samples the 14 mesh screening may be omitted. After everything but metallics has been put through the 20 mesh screen, weigh the minus 4 plus 20 metallics and add the same weight of ground barren quartz to the screened sample. Mix by rolling and cut down the 20 mesh sample with a sample splitter, or otherwise, to the smallest amount compatible with the estimated assay grade of the sample. For low-grade samples, 150 grams is sufficient; 500 grams is usually enough for a high-grade sand. Next grind the small sample through successively finer screens to at least 100 mesh. High-grade samples should be ground to 200 mesh if possible. This will be the most difficult stage of the grinding, as the sample will now contain many individual crystals of extremely hard and tough minerals such as garnet, corundum, spinel, etc.

The minus 20 plus 200 mesh metallics are weighed, and the same weight of ground barren quartz is added to the 200 mesh pulp and mixed by rolling. This pulp may then be assayed by the usual methods, using a flux containing considerable silica. The metallics may be assayed by one of the following methods: The finer metallics, if small in amount, may be scorified. Coarser metallics, if amounting to less than 5 grams, are placed in a 20 gram clay crucible and covered with an equal weight of sulphur. Then, without mixing, put 80 to 100 grams of stock flux into the crucible. This stock flux should contain about 50 percent soda, 40 percent litharge, 5 percent borax glass, 5 percent silica, and 1 percent flour. The fusion may be poured in the usual manner. In most cases the button will be clean, but if unfused iron particles are attached it should be scorified.

The larger samples of coarse metallics may be assayed as follows: Place the entire sample in a 20 gram clay crucible. Add about one-third of its weight of lead, arsenic or antimony in metallic form or as sulphide. Next cover this with a quantity of powdered sulphur equal to the combined weight of the metallics and the other metal added. Without mixing, cover the sulphur with a layer of soda at least one inch in depth. Place cover on crucible. A three inch scorifier, set into the top of the crucible, makes the most satisfactory cover. Place crucible in a cold furnace (muffle type if possible) and bring it slowly to red heat. Remove the covered crucible from furnace, allow it to cool, and weigh. Add an amount of barren quartz sufficient to make the total weight equal to an aliquot fraction of the weight of the sample from which the metallics were obtained. Then crush and grind the entire crucible, contents, cover and added quartz. As a check on this fusion, any metallics found on the screens should be retained and assayed but usually no significant amount of gold will be found in them. It has been found that as much as 100 grams of metallics may be treated in one 20 gram crucible by this method. If the crucible is heated too fast, the sulphur will be volatilized before it can combine with the iron. The presence of lead, arsenic or antimony seems to assist in retarding the volatilization; sulphur quickly volatilizes with no action on the iron. If the metallics are not all attacked, the fusion may be repeated on the residue and the second crucible crushed and added to the first. It will then be necessary to adjust the total weight to a large aliquot fraction.

As an example of the method, suppose a sample weighing ten kilograms is taken. This is crushed to 4 mesh and 20 grams of metallics is left on the screen. These metallics were fused with sulphur, lead and soda as previously explained. After cooling, the crucible, contents and cover were found to weigh 410 grams. Ninety grams of barren quartz was added, and the mixture was crushed and ground through 100 mesh. This 500 grams of pulp is one-twentieth of the weight of the original sample. A sample of this pulp was assayed by usual methods and found to contain 2.40 ounces of gold per ton. This is equivalent to 0.12 ounce per ton when referred to the original sample. About one-fourth gram of metallics was left on the 100 mesh screen when grinding the fusion. This was scorified and found to contain a total of 0.07 milligram of gold, which is insignificant when referred to ten kilograms of sample.

Twenty grams of barren quartz was added to the minus 4 mesh sample to replace the metallics which had been removed. This sample was then reduced to 2,400 grams with a sample splitter. This 2,400 gram sample was next ground to 20 mesh, using an intermediate 8 mesh screen. The minus 4 plus 20 mesh metallics amounted to 80 grams. These metallics were fused in the same manner as the first lot, and the fusion weighed 480 grams. Barren quartz was added to make a total weight of 600 grams, which is one-fourth of the weight of the sample from which they came. After being ground to 100 mesh, this pulp assayed 1.60 ounces per ton of gold, equivalent to 0.40 ounce per ton on the original sample. The metallics left from the last mentioned fusion weighed 0.2 gram and when scorified yielded 0.06 milligram of gold, which was disregarded.

Eighty grams of powdered barren quartz was mixed with the minus 20 mesh sample. The sample was then reduced by splitting to 300 grams. The 300 gram sample was ground to 150 mesh, screening out metallics at 40, 60 and 100 mesh to avoid stalling the grinder. The final grinding was done on the bucking board. The minus 20 plus 150 mesh metallics weighed 1.5 grams. This 1.5 gram lot of metallics was scorified in a three inch scorifier. It contained a total of 2.06 milligrams of gold. Since this was obtained from 300 grams (10.3 assay tons) of sample, it is equivalent to 0.20 ounce per ton on the original sample.

One and five-tenths grams of 150 mesh barren quartz was added to the minus 150 mesh pulp and mixed by rolling. A sample of this pulp was assayed by the usual methods, using a silica flux, and was found to contain 2.76 ounces of gold per ton. The total assay of the original sample is found by adding the items as follows:

	Ounces
Plus 4 mesh metallics, 1/20 of 2.40 ounces	0.12
Minus 4 plus 20 mesh metallics, 1/4 of 1/60	.40
Minus 20 plus 150 mesh metallics, 2.06 divided by 10.3	.20
Final pulp (minus 150 mesh)	2.76
Ounces per ton of gold in original sample	3.48

This example represents a medium-grade black sand. It is not unusual to find samples which yield as much as one-half gram of gold in the final metallics. For this reason, care should be used in handling the metallics to prevent loss of fine scaly particles of gold.

It often happens that no metallics larger than 4 mesh are found, in which case one of the above steps may be omitted. These methods will apply to any screen sizes selected; 4 mesh and 20 mesh have been used here because they seem to be the most convenient sizes for handling the placer concentrates produced in this region.

On account of the repeated screening necessary with black sand samples there is often considerable mechanical loss. It has been found by working with synthetic samples of known value that this does not affect the final assay value as much as would be expected. In other words, the portion of the sample which has been lost has about the same average value as the portion retained. However, calculation affecting the assay value of metallics should be based on the weight of the sample before grinding.

Appendix B

Natural Chemical Elements

Symbol	*Element*	*Atomic Weight*	*Atomic Number*
Ac	Actinium	227	89
Ag	Silver (Argentum)	107.87	47
Al	Aluminum	26.98	13
Ar	Argon	39.95	18
As	Arsenic	74.92	33
At	Astatine	210	85
Au	Gold (Aurum)	196.97	79
B	Boron	10.81	5
Ba	Barium	137.34	56
Be	Beryllium	9.01	4
Bi	Bismuth	208.98	83
Br	Bromine	79.91	35
C	Carbon	12.01	6
Ca	Calcium	40.08	20
[Cb	Columbium	92.91	41]*
Cd	Cadmium	112.40	48
Ce	Cerium	140.12	58
Cl	Chlorine	35.45	17
Co	Cobalt	58.93	27
Cr	Chromium	52.00	24
Cs	Cesium	132.91	55
Cu	Copper (Cuprum)	63.54	29

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*Obsolete name for Niobium (Nb).

Symbol	*Element*	*Atomic Weight*	*Atomic Number*
Dy	Dysprosium	162.50	66
Er	Erbium	167.26	68
Eu	Europium	151.96	63
F	Fluorine	19.00	9
Fe	Iron (Ferrum)	55.85	26
Fr	Francium	223	87
Ga	Gallium	69.72	31
Gd	Gadolinium	157.25	64
Ge	Germanium	72.59	32
H	Hydrogen	1.008	1
He	Helium	4.00	2
Hf	Hafnium	178.49	72
Hg	Mercury (Hydrargyrum)	200.59	80
Ho	Holmium	164.93	67
I	Iodine	126.90	53
In	Indium	114.82	49
Ir	Iridium	192.2	77
K	Potassium (Kalium)	39.10	19
Kr	Krypton	83.80	36
La	Lanthanum	138.91	57
Li	Lithium	6.94	3
Lu	Lutetium	174.97	71
Mg	Magnesium	24.31	12
Mn	Manganese	54.94	25
Mo	Molybdenum	95.94	42
N	Nitrogen	14.01	7
Na	Sodium (Natrium)	22.99	11
Nb	Niobium	93.1	41
Nd	Neodymium	144.24	60
Ne	Neon	20.18	10
Ni	Nickel	58.71	28
O	Oxygen	16.00	8
Os	Osmium	190.2	76
P	Phosphorus	30.97	15
Pa	Protactinium	231	91
Pb	Lead (Plumbum)	207.19	82
Pd	Palladium	106.4	46
Po	Polonium	210	84
Pr	Praseodymium	140.91	59
Pt	Platinum	195.09	78
Ra	Radium	226	88

Symbol	*Element*	*Atomic Weight*	*Atomic Number*
Rb	Rubidium	85.47	37
Re	Rhenium	186.2	75
Rh	Rhodium	102.91	45
Rn	Radon	222	86
Ru	Ruthenium	101.07	44
S	Sulphur	32.06	16
Sb	Antimony (Stibium)	121.75	51
Sc	Scandium	44.96	21
Se	Selenium	78.96	34
Si	Silicon	28.09	14
Sm	Samarium	150.35	62
Sn	Tin (Stannum)	118.69	50
Sr	Strontium	87.62	38
Ta	Tantalum	180.95	73
Tb	Terbium	158.92	65
Te	Tellurium	127.60	52
Th	Thorium	232.04	90
Ti	Titanium	47.90	22
Tl	Thallium	204.37	81
Tm	Thulium	168.93	69
U	Uranium	238.04	92
V	Vanadium	50.94	23
W	Tungsten (Wolframium)	183.85	74
Xe	Xenon	131.30	54
Y	Yttrium	88.91	39
Yb	Ytterbium	173.04	70
Zn	Zinc	65.37	30
Zr	Zirconium	91.22	40

Appendix C

Some Metallic Salts and Their Contents

Salt	*Formula*	*% of Metal*
Aluminum Chloride	$AlCl_3 \cdot 6H_2O$	11.1
Aluminum Chloride (anhydrous)	$AlCl_3$	20.3
Aluminum Sulphate	$Al_2(SO_4)_3 \cdot 18H_2O$	8.1
Antimony Trichloride	$SbCl_3$	53.4
Arsenic Trioxide	As_2O_3	75.9
Cadmium Chloride	$2CdCl_2 \cdot 5H_2O$	49.3
Cadmium Cyanide	$Cd(CN)_2$	68.3
Cadmium Oxide	CdO	87.5
Cadmium Sulphate	$3CdSO_4 \cdot 8H_2O$	43.3
Chloroplatinic Acid	$H_2PtCl_6 \cdot 6H_2O$	37.7
Chromic Trioxide	$CrO_3 \cdot H_2O$	52.0
Cobalt Chloride	$CoCl_2 \cdot 6H_2O$	24.8
Cobalt Sulphate	$CoSO_4 \cdot 7H_2O$	21.0
Copper Acetate	$Cu(CH_3CO_2) \cdot H_2O$	32.0
Copper Carbonate (basic)	$CuCO_3 \cdot Cu(OH)_2$	57.5
Copper Chloride (cupric)	$CuCl_2 \cdot 2H_2O$	37.3
Copper Cyanide (cuprous)	$CuCN$	71.0
Copper Fluoborate	$Cu(BF_4)_2$	26.8
Copper Potassium Cyanide	$K_2Cu(CN)_3$	26.3
Copper Pyrophosphate	$Cu_2P_2O_7$	42.3
Copper Sodium Cyanide	$Na_2Cu(CN)_3$	26.3
Copper Sulphate	$CuSO_4 \cdot 5H_2O$	25.5
Ferric Chloride	$FeCl_3 \cdot 6H_2O$	20.6
Ferric Chloride (anhydrous)	$FeCl_3$	34.5

Salt	*Formula*	*% of Metal*
Ferric Sulphate (anhydrous)	$Fe_2(SO_4)_3$	27.9
Ferrous Ammonium Sulphate	$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	14.2
Ferrous Chloride	$FeCl_2 \cdot 4H_2O$	28.1
Ferrous Sulphate	$FeSO_4 \cdot 7H_2O$	20.1
Gold Chloride (auric)	$AuCl_3 \cdot 2H_2O$	58.1
Gold Cyanide (aurous)	$AuCN$	88.3
Gold Potassium Cyanide	$KAu(CN)_2$	68.3
Gold Sodium Cyanide	$NaAu(CN)_2$	72.5
Indium Chloride	$InCl_3$	51.8
Indium Cyanide	$In(CN)_3$	59.4
Indium Sulphate	$In_2(SO_4)_3$	33.7
Lead Carbonate (basic)	$2PbCO_3 \cdot Pb(OH)_2$	80.1
Lead Fluoborate	$Pb(BF_4)_2$	54.4
Nickel Acetate	$Ni(CH_3CO_2)$	33.2
Nickel Ammonium Sulphate	$NiSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	14.9
Nickel Carbonate (basic)	$2NiCO_3 \cdot 3Ni(OH)_2 \cdot 4H_2O$	50.0
Nickel Chloride	$NiCl_2 \cdot 6H_2O$	24.7
Nickel Cyanide	$Ni(CN)_2 \cdot 4H_2O$	32.1
Nickel Fluoborate	$Ni(BF_4)_2$	25.3
Nickel Sulphaminate	$Ni(NH_2SO_3)_2$	23.4
Nickel Sulphate	$NiSO_4 \cdot 6H_2O$	22.3
Palladium Chloride	$PdCl_2$	60.0
Palladium Diaminodinitrite	$Pd(NH_3)_2(NO_2)_2$	45.8
Platinum Chloride	$PtCl_4 \cdot 5H_2O$	45.7
Platinum Diaminodinitrite	$Pt(NH_3)_2(NO_2)_2$	60.8
Potassium Stannate	$K_2SnO_3 \cdot 3H_2O$	39.6
Rhodium Chloride	$RhCl_3 \cdot 3H_2O$	39.1
Rhodium Sulphate	$Rh_2(SO_4)_3$	20.8
Silver Chloride	$AgCl$	75.2
Silver Cyanide	$AgCN$	80.5
Silver Nitrate	$AgNO_3$	63.5
Silver Oxide	Ag_2O	93.3
Silver Potassium Cyanide	$KAg(CN)_2$	54.2
Silver Sodium Cyanide	$NaAg(CN)_2$	59.0
Silver Sulphate	Ag_2SO_4	34.6
Sodium Stannate	$Na_2SnO_3 \cdot 3H_2O$	44.5
Sodium Tungstate	$Na_2WO_4 \cdot 2H_2O$	55.8
Tin Chloride (stannous)	$SnCl_2 \cdot 2H_2O$	52.6
Tin Fluoborate (stannous)	$Sn(BF_4)_2$	40.6
Tin Sulphate (stannous)	$SnSO_4$	55.3
Tungstic Acid	H_2WO_4	73.6

Salt	*Formula*	*% of Metal*
Tungstic Oxide	WO_3	79.3
Zinc Carbonate	$ZnCO_3$	52.2
Zinc Chloride	$ZnCl_2$	48.0
Zinc Cyanide	$Zn(CN)_2$	55.7
Zinc Fluoborate	$Zn(BF_4)_2$	27.3
Zinc Oxide	ZnO	80.3
Zinc Pyrophosphate	$Zn_2P_2O_7$	42.9
Zinc Sulphate	$ZnSO_4 \cdot 7H_2O$	22.7
Zinc Sulphate (anhydrous)	$ZnSO_4$	40.4
Zinc Sulphate (exsiccated)	$ZnSO_4 \cdot H_2O$	36.5

Glossary

Absolute: Independent, not arbitrary.

Absolute Alcohol: 99% pure ethanol (ethyl alcohol—C_2H_5OH) by weight.

Absorption (of gases): The solution of gases in a liquid or solid.

Accelerator (chemical): Any substance that causes an increase in the rate of a chemical reaction, such as a catalyst.

Accumulator: Any device capable of storing energy, such as a lead acid storage battery.

Acetamide (CH_3CONH_2): A water-soluble, white, crystalline solid used as a solvent.

Acetate: A salt or ester of acetic acid. Acetate ions (CH_3COO^-) have a single negative charge.

Acetic Acid (CH_3COOH_2): The acid contained in vinegar—a colorless, corrosive liquid with a pungent odor. At low temperature, it solidifies to form glacial acetic acid.

Acetone [$(CH_3)_2CO$]: A volatile, inflammable, colorless, water-soluble liquid used as a solvent; dimethylketone.

Acetylene (C_2H_2): Ethyne—a colorless, inflammable gas produced by the action of water on calcium carbide (CaC_2) and used as a reagent and as a welding gas. When acetylene is burned with oxygen, temperatures can reach 3300°C.

Acid: A substance that liberates hydrogen ions in solution. The hydrogen in an acid can be replaced by a metal to produce a salt of that metal. An acid is the opposite of a base; it turns litmus red.

Acid Radical: A molecule of acid without the acidic hydrogen, such as the sulphate (—SO_4) in sulphuric acid (H_2SO_4). The bivalent sulphate radical (also expressed as SO_4^{2+}) is present in all sulphates.

Acid Salt: The solution produced when only a part of an acid's hydrogen is replaced by a metal. Examples are copper sulphate ($CuSO_4 \cdot 5H_2O$) and cobalt sulphate ($CoSO_4 \cdot 7H_2O$).

Acid Value: The value or measure of the amount of acid in an oil or fat, usually expressed in milligrams. It is determined by checking how many milligrams of a base (sodium hydroxide) are required to neutralize the free acid in one gram of the oil or fat.

Acidic: Having the properties of an acid.

Acidic Hydrogen: The portion of the hydrogen in an acid that is replaced by metal in the formation of a metallic salt.

Acidimetry: The determination of the amount of acid in a solution by titration of the liquid with a base to a neutral end point, usually with a standard solution of sodium hydroxide (NaOH).

Acidolysis: Any method in which hydrolysis is caused by an acid.

Activated Carbon: Carbon (charcoal) that has been treated with steam or a solvent to remove hydrocarbons, making it more absorbent. Activated coconut shell charcoal is considered among the finest of activated carbons. Activated carbon is used to extract values from cyanide solutions, and also as a primary material in filters.

Active Mass: The molecular concentration of a substance under consideration.

Adiabatic (of a reaction): Taking place without heat entering or leaving the system.

Aerobic: In the presence of free oxygen.

Affinity: The attractive force that binds atoms together; their chemical attraction.

Alcohols: A wide range of organic compounds derived from hydrocarbons.

Aliquots: In assaying and inquartation, small pieces of metal (silver, gold, or copper), each of which is marked as to its weight in grams and its purity.

Alkali: A soluble hydroxide of a metal, and in particular of one of the alkali metals, such as sodium; any substance capable of neutralizing an acidic substance, compound, or solution; a base.

Alkali Metals: The univalent metals lithium, sodium, potassium, rubidium, cesium, and francium.

Allo-: A chemical prefix meaning "other."

Allotropy: A property of certain chemical elements of existing in two or more forms that differ in physical properties. Sulphur, for example, can exist in a number of different allotropic forms.

Alloy: A composition (in the form of an intimate mixture, not a compound) of two or more metals. Red brass is an alloy of copper, tin, lead, and zinc.

Alluvial: Deposited by the flowing waters of rivers or streams: for example, alluvial gold. Gold found in dry stream beds is still referred to as alluvial gold.

Alum [$K_2SO_4 \cdot Al_2(SO_4)_3$]: Crystalline potassium aluminum sulphate.

Alumina (Al_2O_3): Aluminum oxide. Alumina occurs in a natural crystalline form called corundum.

Amalgam: A mixture of mercury and gold, silver, or copper. It is commonly listed as an alloy but is more accurately classified as an intimate mixture.

Amalgamation: The process in which mercury is used as a collector of gold or silver.

Ammeter: An electrical meter used to measure the amperage (current) in an electric circuit.

Ammonia (NH_3): A soluble gas. When dissolved in water, ammonia forms an alkaline, pungent solution, ammonium hydroxide (NH_4OH).

Ammonium Chloride (NH_4Cl): Sal ammoniac, a water-soluble, white, crystalline powder used as a reagent.

Ammonium Hydroxide (NH_4OH): The solution formed when ammonia (NH_3) is dissolved in water.

Amorphous: Noncrystalline; having no definite form or shape. Glass is an amorphous material.

Ampere: An electric current of 6×10^{18} electrons (1 coulomb) per second.

Amphiboles: Complex silicate materials.

Anaerobic: In the absence of free oxygen.

Analysis: Any method of determining the composition of substances.

Anhydride: A substance that combines chemically with water to form a more complex substance. A metallic oxide (the anhydride) forms a base with water: sodium oxide (Na_2O) + water (H_2O) = sodium hydroxide ($2NaOH$). A nonmetallic oxide (the anhydride) forms an acid with water: sulphur trioxide (SO_3) + water (H_2O) = sulphuric acid (H_2SO_4).

Anhydrous: Without water, as for example a salt lacking the water of hydration. Hydrous ferric chloride ($Fe_2Cl_3 \cdot 6H_2O$) is an iron chloride salt with its water of hydration; anhydrous ferric chloride (Fe_2Cl_3) is iron chloride salt without its water of hydration.

Anion: A negatively charged ion.

Annealing: Heating to relieve internal strains in a metal that were caused by working it.

Anode: The positive electrode of a DC circuit.

Anti-: A prefix denoting "opposite."

Apatite: Calcium fluophosphate ($Ca_5FP_3O_{12}$)—a naturally occurring mineral.

Aperture: An opening.

Aqua Fortis: "Strong water"—nitric acid (HNO_3).

Aqua Regia: "Royal water"—a solution of from one part nitric acid and one part hydrochloric acid to one part nitric acid and four parts hydrochloric acid. The usual composition is one part nitric acid and three parts hydrochloric acid.

Aqueous: Watery. An aqueous solution is one in which water is the solvent.

Argentiferous: Silver-bearing.

Argol: A crude tartar, potassium hydrogen tartrate; a sediment from wine.

Arsenate: A salt or ester of arsenic acid.

Asbestos: A fibrous amphibole, calcium magnesium silicate.

Aspirator: The apparatus used to draw a current of air or gas through a liquid.

Assay Ton (A.T.): A unit of weight equal to 29.16666 g. Each milligram of weight in a bead from a fire or scorification assay of a sample weighing one assay ton is equal to 1 ounce per ton. Common multiples and subdivisions of the assay ton:

2 A.T. = 58.3333 g
4 A.T. = 116.6666 g
⅓ A.T. = 9.7222 g

⅙ A.T. = 4.8611 g
⅒ A.T. = 2.9166 g
1⁄20 A.T. = 1.4583 g

-ate: A suffix used to indicate a salt created from a relatively high-valence "-ic" acid. For example, "sulphate" identifies a salt of sulphuric acid.

Atom: The smallest portion of an element that retains all of the element's characteristics and that can take part in a chemical reaction.

Atomic Weight: Relative atomic mass.

Atto-: A prefix meaning "one million million millionth."

Auric: Containing trivalent gold (Au^{3+}).

Auric Chloride ($AuCl_3$): Gold chloride—a crystalline, yellow to red, water-soluble salt.

Auriferous: Gold-bearing.

Aurous: Containing univalent gold (Au^{+}).

Azote: Old name for nitrogen.

Azurite: Natural copper carbonate [$Cu(CO_3)_2(OH)_2$].

Baking Soda: Sodium bicarbonate ($NaHCO_3$)—the familiar white, crystalline, water-soluble powder.

Balance: A weighing apparatus.

Base: A substance that reacts with an acid to form a salt and water only. A base is the opposite of an acid; it turn litmus blue.

Base Exchange: Cation exchange.

Base Metals: Metals that are not noble. Characteristically, base metals will tarnish or oxidize in the presence of oxygen (in the air), heat, and moisture.

Basic: Having the properties of a base.

Baume Scale: A scale of specific gravity for liquids (used in hydrometers).

Bauxite: Hydrated aluminum oxide, the principle ore of aluminum.

Bentonite: A clay material similar to fuller's earth that expands when wetted; it is used as a binder in foundry sands, as a drilling mud, and for many other purposes.

Bi-: Prefix denoting "two."

Bicarbonate: A salt of carbonic acid (H_2CO_3).

Binary Compound: A chemical compound consisting of two elements or radicals. In the compound calcium carbide, for example, the suffix "-ide" indicates that it is a binary compound of calcium and carbon.

Bittern: The solution remaining after the crystallization of a salt.

Bivalent: Carrying two positive or negative charges.

Black Ash: Impure sodium carbonate.

Black Lead: Plumbago, graphite—not lead at all, but native carbon.

Blende (zinc blende) (ZnS): A natural zinc sulphate, also known as sphalerite.

Blow Pipe: A device for supplying fresh oxygen to a heat source in order to produce a jet of flame.

Blue Stone: Cupric sulphate ($CuSO_4 \cdot 5H_2O$); also called blue vitriol.

Bone Ash: Calcium phosphate [$Ca_3(PO_4)_2$], obtained by calcining bone in open air.

Bone Black: Animal bone charcoal, obtained by calcining bone in a closed container.

Boric Acid (H_3BO_3): A white, crystalline acid.

Brass: Any of a large class of principally copper and zinc alloys—a base metal alloy.

Brimstone: Blocks or rolls of cast sulphur.

Brinell Hardness Number: A number that represents the impressibility of a particular metallic material by an indenting tool bearing a known weight.

Bromate: A bromic acid salt.

Bromic Acid ($HBrO_3$): A relatively unstable acid, maintained in dilute solutions.

Buchner Funnel: A funnel, usually made of porcelain with an internal perforated filter, used for vacuum-assist filtering.

Calcination: The process of heating strongly or roasting a substance in order to oxidize it.

Calcite: Calcium carbonate ($CaCO_3$).

Caliche: One of a number of salt-impregnated sand or clay surface deposits. One of the chief caliche salts is an impure sodium nitrate ($NaNO_3$), Chile saltpeter.

Calomel: Mercurous chloride (Hg_2Cl_2).

Calx: The metal oxide formed by roasting an ore containing an oxidizable metal value.

Carbon Dioxide (CO_2): Carbonic acid gas.

Carbon Monoxide (CO): A colorless, odorless, very poisonous gas.

Carbonate: A salt of carbonic acid (H_2CO_3).

Caro's Acid (H_2SO_5): Persulphuric acid, as opposed to sulphuric acid (H_2SO_4).

Carrier: A substance that assists in a chemical reaction without itself undergoing any chemical change—a catalyst.

Catalyst: A substance that alters the rate of a chemical reaction (slowing it down or speeding it up) but does not itself become part of the reaction.

Cation: A positively charged ion.

Caustic: Corrosive to organic materials.

Caustic Potash: Potassium hydroxide (KOH).

Caustic Soda: Sodium hydroxide (NaOH).

Celsius (C): Temperature as measured on the centigrade scale devised by Anders Celsius, on which 0° is the melting point of ice, and 100° is the boiling point of water.

Chalk: A natural calcium carbonate ($CaCO_3$).

Chemical Change: A change in a substance involving the alteration of its chemical composition.

Chemical Energy: Energy released from within an atom or molecule by a chemical reaction.

Chlorate: A salt of chloric acid.

Chloric Acid ($HClO_3$): A hypothetical acid, existing in solution.

Chlorine (Cl): A greenish yellow, poisonous, gaseous element with a choking, irritating smell.

Chlorite: A salt of chlorous acid.

Chloroform ($CHCl^3$): A colorless, volatile liquid used as an anaesthetic and as a solvent.

Chloroplatinic Acid ($H_2PtCl_6 \cdot 6H_2O$): A platinum chloride solution; the reddish brown, crystalline substance that dissolves in water to form this solution.

Chlorous Acid ($HClO_2$): A hypothetical acid, existing in solution.

Chromate: A salt of chromic acid (H_2CrO_4).

Cinnabar: Mercuric sulphide (HgS)—the red, solid mercury ore.

Citrate: A salt or ester of citric acid (a complex compound of hydrogen, oxygen, and carbon).

Clathrate Compounds: Chemical compounds that are not formed by a valence bond but by molecular imprisonment, mechanically, due to their lattice-like physical configuration.

Condenser: An apparatus for converting a vapor into a liquid during distillation, usually by reducing the temperature of the vapor to a point below its vaporization temperature.

Copperas: Ferrous sulphate ($FeSO_4$).

Corrosive Sublimate: Mercuric chloride ($HgCl_2$).

Coulomb: The quantity of charge transferred across a conductor in 1 second by a current of 1 ampere.

Cream of Tartar: Potassium hydrogen tartrate ($KHC_4H_4O_6$).

Crucible: A refractory vessel for melting, fusing, or containing high-temperature reactions.

Cryolite: Sodium aluminum fluoride (Na_3AlF_6).

Cupel: A dish, usually made of bone ash, used in cupellation.

Cupellation: The separation of base metals—lead, copper, and so forth—from precious metals by oxidizing the base metals and absorbing the oxides in a cupel, leaving the precious metals behind as a bead on the cupel.

Cupric: Containing bivalent copper (Cu^{2+}), as, for example, cupric salts do.

Cupric Sulphate ($CuSO_4 \cdot 5H_2O$): A transparent, deep blue, crystalline salt.

Cuprous: Containing univalent copper (Cu^+).

Cuprous Oxide (Cu_2O): Cuprite—a reddish crystalline or brown to black granular mineral.

Cyanide: A salt of hydrocyanic acid (HCN); extremely poisonous.

Cyano Group: The univalent —CN radical (CN^-).

Decantation: The separating of a liquid from a solid by letting the solid settle and then carefully pouring off the liquid.

Decinormal Solution: A solution containing one-tenth of a gram equivalent weight of the active component per liter.

Decrepitation: Splitting, bursting apart, or fragmentation of a substance when heated.

Dehydration: Elimination or removal of water.

Deliquescent: Tending to pick up moisture from the air to such an extent as to liquify.

Denature: To poison a substance in order to make it unfit for human consumption, as in the case of denatured alcohol.

Dendrite: A multibranched crystal.

Desiccation: The removal of water to utter dryness.

Destructive Distillation: The carbonization of a complex substance with heat, and the distillation of the volatile substances thereby formed.

Diatomic: Consisting of two atoms per molecule, such as hydrogen gas (H_2).

Dibasic Acid: An acid containing two atoms of acidic hydrogen per molecule, such as sulphuric acid (H_2SO_4).

Diffusion of Solutions: The free movement of molecules or ions of a dissolved substance, producing a uniform concentration of those molecules or ions in the solution.

Dilute: Of concentration of a solute—a solution that contains a large amount of solvent.

Dilution: The act of adding additional solvent to a solution.

DC: Direct current; an electrical current that always flows in the same direction, as opposed to alternating current.

Dissociation: A temporary, reversible decomposition of molecules of a compound in which molecules are split into ions, as in a plating solution or Thum cell.

Distillate: The liquid obtained through condensation of the vapor from a still by the condenser.

Distillation: The process by which a liquid is converted into a vapor in a still and then condensed back into a liquid (the distillate) in a condenser.

Distilled Water: Water that has been purified by distillation.

Dolomite: Pearl spar; calcium magnesium carbonate [$CaMg(CO_3)_2$].

Double Salt: A compound of two salts crystallized from a solution containing both salts.

Effervescence: Small bubbles escaping from a liquid as the result of a chemical action.

Efforescence: The change undergone by some crystals when exposed to air; as the crystals lose some of their water of crystallization, their surface becomes powdery.

Electrode: A conductor by which electric current enters or leaves an electrolyte in electrolysis. The positive electrode is called the anode and the negative electrode is called the cathode.

Electrodeposition: Electroplating, such as that done in a Thum cell.

Electrolysis: Chemical decomposition by an electric current of certain substances that are in a dissolved or molten state.

Electrolyte: A compound in solution or a molten compound that will conduct an electric current.

Electrometallurgy: The field of study dealing with plating, refining, extracting, and forming metals by electrical means.

Elutriation: Classifying, separating, and sizing fine particles of different weights by suspending them in a liquid or air current.

Emulsifying Agent: A substance used to form or stabilize an emulsion.

Emulsion: Small droplets of liquid suspended in another liquid.

End Point: The point at which a reaction is completed—for example, a titration end point or a cupellation end point.

Endothermic: Absorbing heat during a reaction; the opposite of exothermic.

Equation (chemical): The representation with signs and symbols of a chemical reaction, such as $2H_2 + O_2 = 2H_2O$, or $H_2 + Cl_2 = 2HCl$.

Esters: Organic compounds corresponding to inorganic salts.

Ethanol: Ethyl alcohol (C_2H_5OH).

Ethyl Acetate: Acetic ether ($CH_3COOC_2H_5$).

Eutectic Mixture: A solid solution of two or more substances that have been mixed in such proportions that the solution has the lowest freezing point of all the possible mixtures of the components.

Evaporation: Reducing a liquid to a vapor (with or without reaching the liquid's boiling point).

Exothermic: Releasing heat during a reaction; the opposite of endothermic.

Extraction: Separating the desired constituent or constituents from a mixture or compound by distillation, selective solubility, or some other means.

Fahrenheit Scale (F): Temperature scale on which 32° is the melting point of ice, and 212° is the boiling point of water.

Feldspar: Aluminosilicates of potassium, sodium, or calcium.

Ferrate: A salt of ferric acid (H_2FeO_4).

Ferric: Containing trivalent iron (Fe^{3+}).

Ferric Chloride ($FeCl_3 \cdot 6H_2O$): Iron perchloride.

Ferric Oxide (Fe_2O_3): Iron oxide, familiar as rust, but also occurring as hematite.

Ferrite: Any of several types of iron ore.

Ferro-: A prefix denoting "iron."

Filter: A semipermeable device for separating solids from liquids.

Filtrate: The solution left after filtration.

Fineness of Gold: The quantity of gold in an alloy, expressed in parts per thousand. A metal that is 1000 fine is pure gold. An alloy that is 500 fine is half gold and half other metal.

Flint: Impure silica (SiO_3).

Flotation Process: Separation by floating based on the surface tension of water and the relative tendencies of various materials to sink or float.

Flowers of Sulphur: Fine sulphur powder from vapor distillation of crude sulphur.

Fluid Ounce: A unit of measurement equal to 28.41cc.

Flux: A substance used to assist fusion.

Fractional Distillation: Separation of a mixture by collecting the components separately as they boil at different temperatures.

Friable: Easily crumbled.

Fuming Nitric Acid: Nitric acid (HNO_3) containing an excess of nitrogen peroxide (NO_3).

Fused: Combined by being melted together and allowed to solidify.

Galena: Lead sulphide (PbS)—the principal lead ore.

Gallon: Unit of capacity or volume, equivalent to 4.546 L (liter).

Gangue: Useless stony minerals that occur with metallic ores.

Gooch Crucible: A shallow porcelain cup with a perforated bottom; used for filtering.

Halide: A binary compound, one element of which is one of the halogen elements—fluorine, chlorine, bromine, iodine, or astatine.

Hecto-: A prefix denoting 100.

Hepta-: A prefix denoting 7.

Hetero-: A prefix denoting "other" or "different."

Hexa-: A prefix denoting 6.

Holo-: A prefix denoting "whole."

Homo-: A prefix denoting "same."

Homogeneous: Having uniform composition throughout.

Horn Silver: Natural silver chloride (AgCl)—also known as cerargyrite.

Hornblende: Any of several silicates of calcium, magnesium, and iron.

Hydrate: A compound containing chemically combined water of hydration, as opposed to free water. For example, in chloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$), the six water molecules in the formula (the water of hydration of the acid) are chemically combined with the other parts of the acid; they are not free water molecules. Therefore, chloroplatinic acid is a hydrate.

Hydrated: Chemically combined with water; the opposite of anhydrous.

Hydride: A binary compound, one of whose elements is hydrogen.

Hydro-: A prefix denoting "water." In chemical nomenclature, it often denotes a compound of hydrogen, such as hydrochloric acid (HCl).

Hydrochloric Acid: A solution of hydrogen chloride gas (HCl) in water; also called muriatic acid.

Hydrocyanic Acid: A solution of hydrogen cyanide gas (HCN) in water—an intensely poisonous liquid.

Hydrofluoric Acid: A solution of hydrogen fluoride gas (HF) in water.

Hydrogen Ion Concentration: The number of grams of hydrogen ions per liter of a solution.

Hydrogen Peroxide (H_2O_2): A colorless, oily, unstable liquid.

Hydrogen Sulphide (H_2S): Sulphureted hydrogen, prepared by the action of acids on metal sulphides.

Hydrogenate: To combine or treat with hydrogen.

Hydrolysis: Decomposition of a substance by subjecting it to separation in water.

Hydrometer: An instrument used to measure the specific gravity (density) of a liquid by means of a weighted, graduated float.

Hydrophilic: Having an affinity for water, as sodium chloride and various acids have.

Hydroxide: A compound containing the hydroxyl (OH) group, such as sodium hydroxide (NaOH).

Hygro-: A prefix denoting "moisture" or "wet."

Hyper-: A prefix meaning "above" or "beyond."

Hypo-: A prefix denoting "under" or "below."

-ide: A suffix indicating a binary compound composed of only two elements or radicals.

Implosion: The act of collapsing inward.

Inert: Of mineral origin; not containing carbon compounds, which are organic.

Insoluble: Not able to dissolve or go into solution in a particular solvent. Gold is insoluble in water and single acids, but is soluble in aqua regia.

Integer: A whole number.

Interface: The surface that separates matter in two chemical phases.

Intimate Mixture: A mixture that shows a close combination of particles or elements.

Iodate: A salt of iodic acid (HIO_3).

Iodic: Containing pentavalent iodine (I^{5+}).

Iodide: A binary compound, one of whose elements is iodine.

Ion: An electrically charged atom or group of atoms (radical). Cations are positive (+) and anions are negative (–).

Ion Exchange: The process by which certain compounds, while in solution, trade (exchange) ions, or by which certain metals, when immersed in a solution, replace some ions already in solution with ions from themselves.

Ionization: The formation of ions.

-ite: A suffix used to indicate a salt created from a relatively low-valence "-ous" acid. For example, "sulphite" identifies a salt of sulphurous acid.

Kaolin: A fine, white china clay.

Kilo-: A prefix denoting 1000. Kilogram, for example, means 1000 grams.

Leaching: Washing out (dissolving) a soluble constituent from an insoluble matrix—such as leaching gold with cyanide solution.

Lime: Calcium oxide (CaO), a white or grayish white solid that combines with water to form slaked lime—calcium hydroxide (CaOH).

Liquid: The state of matter that is between a solid and a gas.

Litharge: Lead monoxide (PbO).

Litmus: A soluble substance of vegetable origin that is turned red by acids and blue by bases; used as a pH indicator.

Liter: A volume equal to 1000 cc (1 cubic decimeter).

Macro-: A prefix denoting "large."

Magnesite: Magnesium carbonate ($MgCO_3$).

Magnetite: Magnetic iron ore (Fe_3O_4).

Malachite: Copper carbonate [$Cu_2CO_3(OH)_2$].

Maleate: A salt or ester of maleic acid (a complex acid composed of hydrogen, oxygen, and carbon).

Marble: Natural calcium carbonate ($CaCO_3$).

Matte: A mixture of iron and copper sulphides.

Melting Point: The constant temperature at which the solid and liquid phases of a particular substance are at equilibrium at a given pressure.

Meniscus: The curved surface of a liquid in a vessel. If the curve is less than 90° between the liquid and the vessel wall, the meniscus is concave; if the curve is greater than 90°, the meniscus is convex.

Mercuric: Containing bivalent mercury (Hg^{2+}).

Mercuric Chloride ($HgCl_2$): A binary compound of mercury and chlorine; also called corrosive sublimate.

Mercuric Fulminate [$Hg(CNO)_2$]: An explosive mercury compound.

Mercuric Oxide (HgO): A poisonous soluble powder.

Mercuric Sulphide (HgS): Cinnabar—the common mercury ore.

Mercurous: Containing univalent mercury (Hg^+).

Metallurgy: The science and study of metals.

Meter: A unit of length that is equivalent to 39.3701 in.

Metric Ton: A unit of weight equal to 1000 kg or 2,204.61 lbs.

Micro-: A prefix meaning "small"; also used to denote "one-millionth."

Mil: A unit of length equal to one-thousandth of an inch.

Milli-: A prefix denoting "one-thousandth."

Minim: A volume equal to 1/60 dram and equivalent to 0.0591cc.

Minium: Red lead (Pb_3O_4).

Miscible: Capable of being mixed to form a homogeneous mixture. Alcohol and water are completely miscible.

Mispickel: Arsenopyrite ($FeAsS$).

Molarity: An expression of the strength of a solution based on the number of moles of solvent per kilogram of solution.

Molecule: The smallest portion of a substance that can exist stably and independently, and retain all of the substance's properties.

Monohydrate: A hydrate containing only one molecule of chemically combined water.

Muriate: A salt of hydrochloric acid (HCl).

Muriatic Acid: Hydrochloric acid (HCl).

Nano-: A prefix meaning "one thousand-millionth"—that is, one-billionth.

Neutral: Neither acidic nor alkaline (basic).

Neutralization: The process of adding an acid to an alkaline (basic) solution or an alkali (base) to an acidic solution to produce a neutral condition.

Nitrate: A salt of nitric acid (HNO_3).

Niter: Saltpeter, potassium nitrate (KNO_3).

Nitric Acid (HNO_3): A colorless, corrosive, water-soluble acid; aqua fortis.

Nitric Oxide (NO): A colorless gas that reacts with oxygen on contact to form nitrogen dioxide (NO_2), a corrosive gas with brown fumes. Nitric oxide is formed by the reaction of nitric acid with metal.

Nitrification: The treatment of an element with nitric acid.

Nitrite: The salt or ester of nitrous acid (HNO_2).

Nor-: A chemical prefix meaning "normal."

Oleum: Pyrosulphuric acid ($H_2S_2O_7$)—a concentrated sulphuric acid containing an extra sulphur trioxide (SO_3). Oleum is very hygroscopic (water-attracting), and makes an excellent dehydrating agent.

Olivine: Magnesium iron silicate [$(Mg,Fe)_2SiO_4$].

Ore: A naturally occurring mineral containing a metal or nonmetal value, such as sulphur, copper, or gold.

Organic Compounds: Chemical compounds containing carbon combined with hydrogen (hydrocarbons).

Osmic Acid: Osmium tetroxide (OsO_4).

Osmiridium: A natural alloy of osmium and iridium; also called iridosmine.

Osmosis: The flow of a solvent or water through a semipermeable membrane.

Ounce (avoirdupois): A weight equal to 437½ grains, and equivalent to 28.3 g.

Ounce (fluid): A volume equal to 8 fluid drams, and equivalent to 28.41cc.

Ounce (troy): A weight equal to 480 grains, and equivalent to 31.1 g.

Ox-: A prefix indicating the presence of oxygen as a radical in a compound.

Oxalic Acid [$(COOH)_2 \cdot 2H_2O$]: A poisonous, crystalline, white, water-soluble acid.

Oxidant: The substance that supplies the oxygen in an oxidation reaction.

Oxidation: The process of combining a substance with oxygen or of removing hydrogen from a substance. In an oxidation reaction, a metallic atom loses electrons, so that, for example, bivalent ferrous (Fe^{2+}) atoms become trivalent ferric (Fe^{3+}) atoms.

Oxidation–Reduction (Redox): The simultaneous double reaction, shown separately as oxidize → reduce, reduce → oxidize.

Oxide: A binary compound, one of whose elements is oxygen.

Oxidizing Agent: An agent that accepts electrons and is thereby reduced.

Para-: A prefix meaning "beside," "beyond," "wrong," or "irregular."

Pearlash: Potassium carbonate (K_2CO_3).

Penta-: A prefix denoting 5.

Per-: A prefix indicating an excess of the normal amount; for example, hydrogen peroxide (H_2O_2) possesses an extra or excess oxygen atom.

Peri-: A prefix denoting "around" or "about."

Peroxide: An oxide that yields hydrogen peroxide when combined with an acid.

Persulphuric Acids: Acids such as Caro's acid (H_2SO_5) and peroxydisulphuric acid ($H_2S_2O_8$) that contain extra oxygen or sulphate groups.

pH: A measure based on hydrogen ion concentration in a solution—a key to the relative acidity or basicness (alkalinity) of the solution.

Pico-: A prefix denoting "one-trillionth."

Pint: A volume equal to one-eighth of a U.S. gallon.

Plaster of Paris: Powdered calcium sulphate ($CaSO_4 \cdot 2H_2O$).

Platinic: Containing tetravalent platinum (Pt^{4+}).

Platinous: Containing bivalent platinum (Pt^{2+}).

Platinum Chloride Solution: Chloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$).

Potash: Potassium carbonate (K_2CO_3); also applied loosely to caustic potash (KOH).

Potassium Bicarbonate: Potassium hydrogen carbonate ($KHCO_3$).

Potassium Nitrate (KNO_3): Saltpeter.

Power Alcohol: Ethanol.

Precipitate: An insoluble substance formed in a solution as the result of a chemical reaction.

Precipitation: The formation of a precipitate.

Proof Spirit: Ethanol that is 49.28% alcohol by weight.

Propane ($CH_3CH_2CH_3$): A colorless, inflammable gas used as a fuel; also called dimethylmethane.

Prussic Acid: A solution of hydrocyanic acid (HCN)—extremely poisonous.

Purine ($C_5H_4N_4$): An organic base related to uric acid.

Purple of Cassius: A mixture of colloidal gold and stannic acid. This is the product produced when gold chloride is tested with stannous chloride for gold in the spot plate.

Pyrex: The trade name for a heat-resistant glass widely used in chemical ware.

Pyrites: Natural sulphides of certain metals such as iron pyrite (FeS_2) and fool's gold ($CuFeS_2$), a copper iron sulphite.

Pyro-: A prefix denoting "fire," "strong heat," or—for various substances that are produced by heat—"heating" or "fusion." For example, boric acid, when heated, produces what is called pyroboric acid.

Pyrolusite: A natural manganese dioxide (MnO_2).

Pyrolysis: Chemical decomposition caused by the action of very high heat.

Pyrosulphuric Acid ($H_2S_2O_7$): Oleum.

Pyrotechnics: Fireworks, explosives.

Qualitative: Dealing with the nature of substances as opposed to the amounts of their components.

Quantitative: Dealing with the amounts of, as well as the nature of, the components of a substance under consideration.

Quantum: A discrete unit of energy.

Quart: A volume equal to one-quarter of a U.S. gallon.

Quartz: Natural crystalline silica—silicon dioxide (SiO_2).

Quicklime: Calcium oxide (CaO).

Quicksilver: An old term for mercury (Hg).

Raffinate: The refined liquid remaining after a solvent extraction.

Reagent: A chemical substance used to bring about a chemical reaction.

Red Lead (Pb_3O_4): Minium.

Redox: An oxidation—reduction reaction and the simultaneous reverse reaction.

Reducing Agent: An agent that removes oxygen; one that donates electrons during a reaction and thereby becomes oxidized.

Reduction: A process that removes oxygen from (reduces) a substance.

Refine: To purify.

Reflux: To flow back (ebb), as in a reflux condenser.

Refractory: Able to withstand extreme, elevated heating without damage or physical alteration.

Refrigerant: A fluid that vaporizes at a low temperature, such as Freon or ammonia, used in refrigeration devices.

Retort: Any vessel in which a chemical reaction takes place; especially a still used for distillation.

Reversible Reaction: A chemical reaction that can be undone, or made to go in either direction, as $NH_3 + H_2O \rightarrow NH_4^+ + OH^-$ can be reversed to $NH_4^+ + OH^- \rightarrow NH_3 + H_2O$.

Rust: Hydrated oxide of iron ($Fe_2O_3 \cdot H_2O$).

Sal Ammoniac: Ammonium chloride (NH_4Cl).

Saline: Containing a salt, such as sodium chloride (NaCl).

Salt: A chemical compound formed when the hydrogen of an acid is replaced by a metal. For example, sodium (metal) will replace the hydrogen in hydrochloric acid (HCl) to form table salt, sodium chloride (NaCl).

Saturated Compound: A compound that cannot form additional compounds because it lacks free valence electrons.

Saturated Solution: A solution that exists in equilibrium with the maximum normal quantity of solute.

Scheele's Green: Copper arsenite ($CuHAsO_3$), a bright green water-soluble powder.

Scruple: A weight equal to $\frac{1}{24}$ of a troy ounce.

Selenate: A salt or ester of selenic acid (H_2SeO_4).

Silica: Silicon dioxide (SiO_2).

Silicate: A salt of silicic acid (H_2SiO_3). Silicates are usually considered to be compounds of silica and the oxide of whatever metal is present.

Silver Bromide (AgBr): A water-insoluble yellowish powder that darkens when exposed to light.

Silver Chloride (AgCl): Cerargyrite, silver horn—a white water-insoluble powder that darkens when exposed to light.

Silver Iodide (Agl): A pale yellow, water-insoluble solid that darkens when exposed to light.

Silver Nitrate ($AgNO_3$): A white, crystalline, water-soluble powder.

Slag: The nonmetallic material obtained during smelting of metallic ores.

Soda Lime: A mixture of sodium hydroxide (NaOH) and calcium hydroxide (CaOH).

Sodium Chlorate ($NaClO_3$): A water-soluble colorless solid.

Sodium Cyanide (NaCN): The cyanide compound most commonly used in plating, fumigation, and ore extraction; it is extremely poisonous.

Sodium Nitrate ($NaNO_3$): Saltpeter.

Sodium Peroxide (Na_2O_2): A water-soluble, yellowish white powder that is a strong oxidizing agent.

Solubility: The extent to which a solute will dissolve in a solvent.

Solute: A substance that dissolves in a solvent.

Solvent: A fluid having the power to dissolve certain substances (solutes) in it.

Specific Gravity (SG): Relative density of a substance to the density of water.

Specific Volume: The reciprocal of a substance's density at a given temperature.

Spelter: 97% pure zinc.

Spirits of Salt: A solution of hydrochloric acid (HCl).

Stabilization: Preventing chemical decomposition of a substance by using a negative catalyst or by adding a stabilizer.

Stannate: A stannic acid salt.

Stannic: Containing tetravalent tin (Sn^{4+}).

Stannic Acid: One of various acids created by compounding stannic oxide (SnO_2) with water (H_2O).

Stannous: Containing bivalent tin (Sn^{2+}).

Stannum: Old term for tin.

Still: Apparatus used for distilling.

Sub-: Prefix meaning "under" or "below."

Sublimate: A solid obtained by direct solidification of a vapor, without its pressing through a liquid state.

Sublimation: The process of going from a solid to a vapor without melting.

Sugar of Lead: Lead acetate [$Pb(C_2H_3O_2)_2 \cdot 3H_2O$]—a poisonous, white, crystalline, water-soluble solid.

Sulphate: A salt or ester of sulphuric acid (H_2SO_4).

Sulphide: A binary compound, one of whose elements is sulphur.

Sulphite: A salt or ester of sulphurous acid (H_2SO_3).

Sulphur Dioxide (SO_2): A colorless, water-soluble, suffocating gas.

Sulphuric Acid (H_2SO_4): Vitriol, oil of vitriol.

Supersaturated Solution: A solution that contains an excess (beyond saturation point) of solute in dissociated form.

Talc: Hydrated magnesium silicate [$H_2Mg_3(SiO_3)_4$].

Tera-: A prefix denoting "one million million."

Ternary Compound: A compound consisting of three different elements or groups, such as HNO_3 (nitric acid).

Tetra-: Prefix denoting 4.

Tetrad: An element that has a valence of 4.

Thio-: A prefix denoting "sulphur"—used in naming various sulphur compounds, such as thiosulphuric acid ($H_2S_2O_3$).

Tincture: An alcohol extract or a solution in alcohol, such as tincture of iodine.

Titration: A method used in volumetric analysis of adding measured amounts of a solution with a burette to a definite amount of another solution, until an end point is reached.

Toxic: Poisonous.

Toxin: An intensely poisonous compound.

Triad: An element that has a valence of 3.

Univalent: Carrying a single positive or negative charge.

Unstable: Easily decomposed.

Vacuum: A volume of space containing no molecules or atoms.

Vacuum Distillation: Distillation under reduced pressure. The reduced pressure in the still lowers the boiling temperature of the substance to be distilled, allowing you to distill substances that would decompose at normal pressures.

Valence: The chemical combining power of an atom.

Volatile: Having a high vapor pressure; passing readily from solid or liquid to a vapor.

Water Glass: Sodium silicate (Na_2SiO_3).

Water of Hydration: The water chemically involved in the structure of a compound (rather than simply diluting the compound).

Wetting Agent: A substance used to lower the surface tension of a fluid.

White Lead: Lead carbonate ($PbCO_3$).

Zeolite: Hydrated silicate of calcium and aluminum.

Zinc White: Zinc oxide (ZnO).

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