DEVELOPMENTS IN
MINERAL PROCESSING

16

THE METRICS OF MATERIAL AND METAL ECOLOGY

HARMONIZING THE RESOURCE, TECHNOLOGY AND ENVIRONMENTAL CYCLES

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Preface

Rapid growth of the world economy is straining our sustainable use of the Earth's natural resources. This makes the economic reuse and recycling of materials and end-of-life products extremely important in the future. Natural Laws, engineering and economics make the closure of the material cycles possible, however also have its limitations.

Metal and Material Ecology links the principles of Industrial Ecology to the fundamentals of separation physics and thermodynamics in the unit operations that close the material cycle. In a unique blend of theory and industrial practice it is explained how to keep second generation materials in the material cycle. This is the product of the authors' research over the past number of years in which recycling theory was developed. Therefore, this book provides an excellent basis to continue research in these areas. It also lays the basis for teaching the fundamental theory of recycling systems and technology to under- and graduate students, linking recycling theory to some aspects of product design - and quantify this in terms of metrics for sustainability. We show how important it is to understand "the bigger picture" of the material and metal production system, the "Web of Metals and Materials" in the context of population balance modelling, fundamental separation physics and thermodynamics. We show that if this is understood the system can be optimized economically and hence a better efficiency can be reached. This is crucial to reaching sustainability in metal and material usage. It also supplies guidelines to the design engineer to show the consequences of poor design.

The book is written in four self-contained parts, that can essentially be read as separate parts. The structure of the parts is such that it also demonstrates the basic philosophy of the book i.e. we move from the systems perspective of Metal and Material Ecology, to the population balance theory of recycling systems and finally to reactor technology of recycling systems. We illustrate everything with numerous simulation models, figures and data. In doing so we would like to provide the reader with all the models and data, available on the included CD rom: i.e. we would like to create a trend of "share-data" to ensure that data is freely available to everyone, ensuring that the system of material recycling can at all times be transparently modelled and optimized economically but also environmentally. We believe this is essential if the beautiful principles of Industrial Ecology are to be realized! This fundamental approach provides a basis for harmonizing and connect the material streams of different industries and hence also level the legislative playing field, with the objective to minimize environmental impact and damage. At the same time it provides a fundamental metric for Design for Recyling and Recovery.

This book is also a result of the philosophy the authors developed for an international MSc course in which they were involved. Many fruitful discussions with the master students have contributed to the contents of this book. They are the carriers of our message into the future, therefore we dedicated this book to them.

The Authors

Something will have gone out of us as a people
if we ever let the remaining wilderness be destroyed,
if we permit the last virgin forest to be turned into comic books and plastic cigarette cases;
if we drive the few remaining members of the wild species into zoos or extinction;
if we pollute the last clean air and dirty the last clean streams,
and push our paved roads through the last of the silence.
so that never again will people be free in their own country from the noise,
the exhausts, the stinks of human and automotive waste,
and so that never again can we have the chance to see ourselves single, separate,
vertical and individual in the world, part of the environment of trees and rocks and soil,
brother to the other animals, part of the natural world and competent to belong in it.
We simply need that wild country available to us,
even if we never do more than drive to its edge and look in,
for it can be a means of reassuring ourselves of our sanity as creatures,
as part of the geography of hope...

Wallace Stegner

Contents

Part I

Introduction

Chapter 1

Harmonizing the resource, technology and environmental cycles

Rapid growth of the world economy is straining our sustainable use of the Earth's natural resources. This makes the economic reuse and recycling of materials and end-of-life products extremely important in the future. Natural Laws, engineering and economics make the closure of the material cycles possible, however also have its limitations.

It is the principle objective of this book to explore the limits of the resource system as a whole on the basis of technology and its principles by applying the systemic approach of Industrial Ecology and provide first principles metrics to measure Design for Recovery and Recycling and approach sustainability in order to minimize environmental impact.

This book bridges the gap between physics and chemistry of the various highly interconnected actors within the Metal and Material Ecology system, linking resources to products and finally to recycled materials. The holistic concepts of ecology are linked to process technology via the first principles governing the phenomena within process reactors and manufacturing plants within the constraints of economics. This fundamental approach provides a basis for harmonizing and connect the material streams of different industries and hence also level the legislative playing field.

These concepts can be summarised into the three cycles depicted by Figure 1.1, symbolically showing the links between three interconnected cycles: the resource cycle, the technology cycle and the life cycle [1, 2, 4, 5, 6, 7]. These have to be among others connected to realize the ambitions of the sustainable use of materials. Therefore, Figure 1.1 is the golden thread or rather, the golden sphere, of this book [3, 8]. The various intersections of Figure 1.1 will be discussed, at which the complex interplay between systems dynamics, (sampling) statistics, separation efficiency (recovery), metallurgical thermodynamics, grade of recycling (intermediate) products, liberation, product design and performance, system architecture, economics etc. will be explored. These intersections will drive the changes. However, there is no possibility to fulfil this task without combining knowledge and technology from the simplest separation and sorting technology to most complex metallurgical reactor optimization via fundamental studies on flow and kinetics in pyrometallurgical reactors, process layout, as well as product design. Moreover, it requires that new and innovative designs and production methods must be developed. This suggests that the optimization of the resource cycle

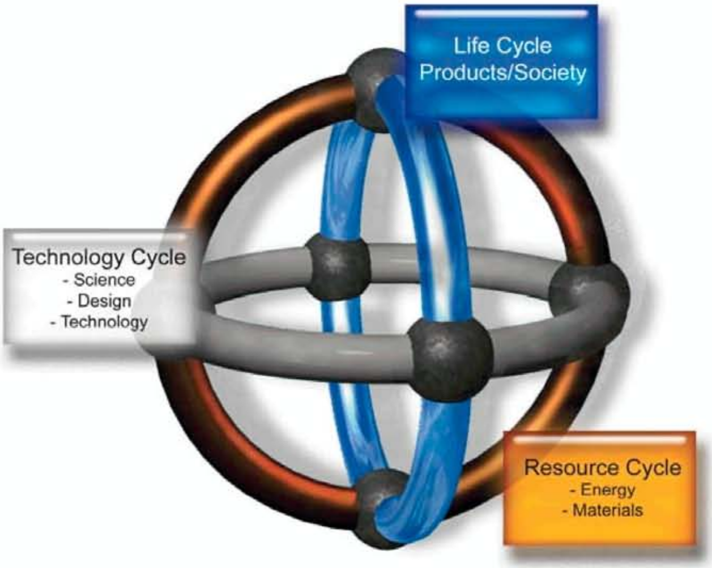

Figure 1.1: Sustainability achieved by linking among others the three depicted cycles and associated disciplines within the resource system [1, 2, 3]

in a world in which products change rapidly is only possible if the interaction between all technological aspects of creating / using / discarding / recycling products is considered in relationship to fundamental studies including environmental control and policy. It is therefore imperative to achieve sustainability change at various system levels, from global material cycles down to plant and process equipment design and operation. The grey plane (horizontal) of the Figure 1.1 represents all technological disciplines involved to achieve this. The golden circle is dealing with complex, large-scale systems of material and energy cycles, where company/plant/sector/product boundaries are crossed. Therefore the process-of-change will involve and affect a great variety of stakeholders represented in the blue circle. These simultaneous interactions between the different cycles in Figure 1.1 have to be orchestrated from a system-engineering point of view, which combines knowledge of processes, production systems, unit operations (mechanical recycling and metallurgical processes) material and energy flows and design with that of economics, social sciences and environmental impact. The designer overlooks often recycling, but legislation makes recycling a very important part of product design. This requires that the link between design software and recycling models can be established in order to predict the recyclability of a product during the design phase, as well as to be able to apply design for recycling on a solid technological basis. To maximize the recycling rate of a product, its resource cycle, consisting of complex interconnected material cycles originating from recycling, has to be optimised from a technological as well as an economical point of view, taking cognisance of environmental impact and legislation as well as design. This optimization for future products, for example the multi-material ultra-light car, requires that the parameters determining the recovery rate for each of the materials present as well as the dynamics and statistically distributed nature of the resource cycle system have to be fully understood. Fundamental knowledge of recycling processes, such as shredding, mechanical separation processes and metallurgy, and material characteristics of recycling (intermediate) products (material type, liberation, etc.) have to be combined with that of the design of the product (material combinations and connections). If Computer Aided Design (CAD) software is to be linked to the calculation and prediction of the recycling rate, a fundamental description of product recycling systems is essential to understand and optimise the resource cycle system. Even legislation needs to consider more fundamental methods and metrics during their formulation. The recycling legislation can be defendably implemented if the knowledge and the tools of the fundamental framework are available to calculate statistically sound recovery and recycling rates. As is indicated by Figure 1.1, a sound technological framework is required to ensure a more sustainable development of our society, in close collaboration with the indicated disciplines in which products have to comply with the recycling targets as imposed by legislation (for example [9]), in combination with constraints on emissions and light weight design, consumer demands and safety regulation. The basic philosophy behind this book is that without a system perspective and a deep theoretical and industrial understanding of technology at the same time, sustainability will be difficult to reach as discussed in the three sections of this book. This closure is to be found in the golden sphere Figure 1.1 detailed by the three cycles:

- **The Sustainability Sphere:** The complete sphere represents all three parts i.e. Part II to Part IV of this book but also more specifically the systems engineering approach, which is more the focus of Part II i.e. the Metal and Material Ecology.

- **Life Cycle:** The link of the metal and material system to the environment is discussed also predominantly in Part II.

- **Resource Cycle:** This cycle is also the topic of Part II but especially the interaction between design, the product and recycling is discussed in more detail in Part III i.e. using the end-of-life vehicles as an example. In addition the resource cycles and systems of the metals Ag, Bi, Cu, Fe, Ni, Pb, PGM's, PM's, Sn, and Zn are also a focus of this work in relationship to the recycling electronic goods.

- **Technology Cycle:** The interaction between design and metallurgy is the focus of Part IV by the discussion of the metallurgical recycling of aluminium. Although the metallurgy of numerous metals are touched on in this book, aluminium is chosen as representing the modern metals, but also its reactivity makes it an interesting one to discuss from a recycling and design perspective.

This book also contains extensive appendices:

- Appendix A discusses the relevant theory such as population balance modelling, thermodynamics of recycling metallurgy and computational fluid dynamics modelling. These are the foundations that holds the sphere and systems models in place.

- Appendix B discusses different metal production and recycling charts.

- Added software of end-life-vehicle recycling models in Appendix C and Appendix D demonstrates the use of all the tools discussed in the book, which all to be found on the accompanying CD rom.

The "Web of Life" is an ancient idea, which has been used by poets, philosophers, and mystics throughout the ages to convey the sense of interwovenness and interdependence of all phenomena [10]. This ancient idea underlies also many of the major problems of today: complex problems that can not be understood in isolation. There are solutions to these "systemic" problems, but they require a radical shift in our tools, our perceptions, our thinking, and our values. The basis for this shift can be found in ecology and systems thinking. Ecologists, "biological system-thinkers", view the web of life as a multidimensional network of ecological communities. By viewing an ecological community as an assemblage of organisms, bound into a functional whole by their mutual relationships, ecologists facilitated the change of focus from organisms to communities and back, applying the same kinds of concepts to different kinds of system levels [10]. This perception is essential to understand the interwovenness and interdependence in the web of life. Based on the examples of metals, this book will show that this view is equally critical to understand our industrial economy, and thus to develop the required tools, thinking, and values. Viable solutions from a systemic perspective are those that are "sustainable". Using industrial ecology - which employs the analogy with ecology to assist the development of "sustainable" industrial systems [11, 12, 13, 14, 15] - it will be shown that to develop and control such industrial systems, co-ordinated actions across all system levels are required. In terms of industrial ecology, we need to understand the "metal ecology": the community of metallurgical reactors, the "industrial organisms", consumer product design, their physical, technological, legislative and economic surroundings and the functional relationships between them. Neither in industrial ecology literature, nor metallurgical literature, models have been developed that can connect the detailed models of engineers and holistic models of industrial ecology, and thus facilitate materialization of industrial ecology concepts. In this book theory and models are developed that connect the different system levels of the metal ecology: from metallurgical reactors to the global metal cycles to products and back. Figure 1.2 gives some indication of this complex web of metals and how these are intricately connected by mineralogy, metallurgy and thermodynamics. It shows which minor and harmful elements are connected to which commodity metal and also shows which metal groups can adequately be processed economically in present facilities. Violating these combinations could lead to problems in recycling of end-of-life products and therefore lead to the loss of valuable metals from the cycle! The metal wheel (Figure 1.2) can provide for a valuable tool to establish the different interdependencies between the production routes of different metals [16]. Estimating the effect of a change in the production of one metal on other metals, however, would call for comprehensive modelling of the interconnected metal production system. Table 1.1 gives the magnitude of the total metal streams per annum (a) which are part of this system suggesting a large impact to nature if recycling is not optimally achieved.

1.1 Sustainability of metals?

The central theme of this book is the sustainability of metal production and use. The sustainable use of metals may seem like a contradiction in terms to many people, as metals are not renewable resources in the biological sense, and are often associated with environmental problems. A productive, economic ore body can be composed of a few parts per million (gold) to a few percent (lead, zinc) metal, with the remainder being residue of little economic value. Consequently, production processes can have undesirable environmental consequences if not properly controlled. As a basis for the discussion on the sustainability of metals, a short introduction on metals and resources are given as well as their economic value. The

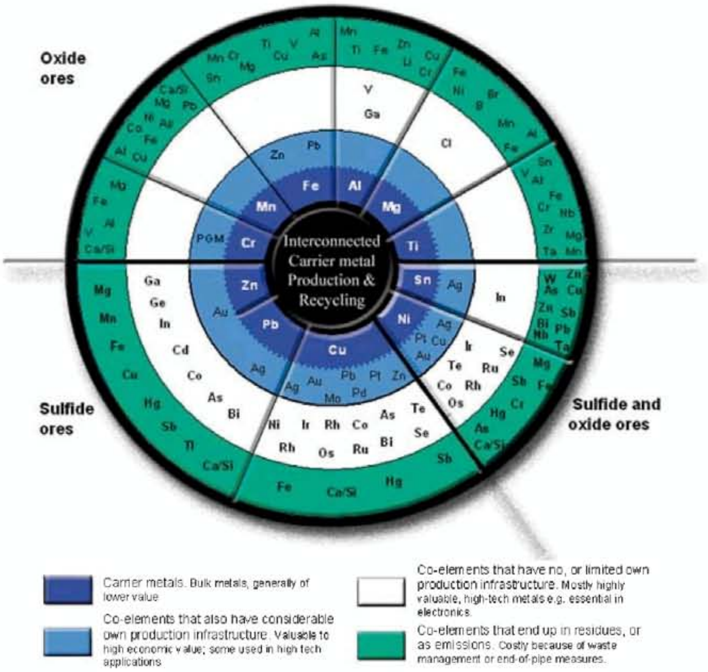

Figure 1.2: "The Metal Wheel": The metal wheel complements Figure 3.3 by showing metal linkages in natural resource processing, illustrating the capacity of available metallurgical processes to deal with impurities in their (primary or secondary) feed. Co-elements are economically and technologically valuable minor elements or impurities found in ores of the carrier metals [7]

Table 1.1: World metal production and recycling 2002 (**USGS http://minerals.usgs.gov**) figures in 10^6metric t. In Appendix B data for various elements are given between the years 1940 to 2000 (source USGS)

Metal	Production	Recycling (%)
Steel	903.6	32
Steel(2003)	964.8	32
Al	25.9	49
Cu	15.5	50
Pb	6.39	45
Zn	8.91	31
Sn	0.278	5
Ag	0.02(mine)	35
Ni	1.21	

glance backward to our past makes it evident that our ancestors recycled metals thousands of years ago. Today we understand why. Pure metals are chemical elements and therefore by definition mon-atomic. To use a simple image: Even if one recycles a copper atom a thousand times it remains always a copper atom with its characteristic properties. It is almost self-explanatory that the fundamental structures of recycling systems can best be demonstrated by metals, which do not change properties when returned into a second usage cycle. Each molecule of plastic material consists of up to several thousands of atoms. The structure of the molecule determines the chemical and physical properties. During utilisation, and even more so, during any thermal processing for reuse, such huge molecules are subject to various forms of destruction on microscopic level, which immediately changes the properties of the "recycled" plastic. This is one of the reasons why plastic is hardly ever recycled without adding fresh virgin material to compensate property deterioration. We deem it therefore inappropriate to use non-metallic, in particular organic material, as typical recycling material, in order to study implications of future recycling activities. Nonetheless, wherever it proved helpful non-metallic materials have been discussed or compared with metals to underline different behaviour and the consequences for recycling systems. Typical example: metals are exclusively subject to material recycling; organic substances are partly reused as fuel because of their remaining heat value. For the sake of transparency this book will intentionally be restricted to metals - in pure or alloyed form - without attempting to write another book on metallurgical processing, for which there are a variety as referenced at appropriate places in this book. On the contrary the intention is to work out common features of the numerous metallurgical processes for the winning of the various base metals, as well as characteristic differences between processes for primary material (ores and concentrates) and those for residual material after passing the first utilisation cycle. Such material, like production scrap, collected (end-of-life) scrap or metalliferous residues, will be collectively called in this book "second generation material" (SGM). As a basis for the discussion on the sustainability of metals, a short introduction on metals and resources is given.

1.1.1 Metals

Life without metals, however, is inconceivable. Metals have been part of human activity since pieces of native copper were first hammered into simple tools about 6000 BC. Today, metals are vital for the production of almost all manufactured products. No aircraft, automobile, computer, or electrical appliance can function without metals. Electrical power supply is dependent on copper and aluminium [17]. For that reason, metals should be included in any overall consideration of sustainability. In addition, metals can in theory be reused countless times, with significant savings in energy and reduction of waste compared to primary processing. Of the ninety-two naturally occurring elements, seventy are metals [17]. Metals in general are characterized by a number of properties including lustre, malleability and the capacity to conduct heat and electricity. The metallic atoms readily lose electrons to form positive ions ("cations"). Chemically, metals are defined according to their position on the Periodic Table, and include different groupings: alkali metals, alkaline earth metals, transition metals, basic metals, and rare earth metals.

Figure 1.3 shows that metals are located on the left side and the middle of the periodic table. Popularly, the name is applied to certain hard, fusible pure metals, including gold, silver, copper, iron, tin, lead, zinc, nickel, and also to the mixed metals, and metallic alloys, such as brass, bronze, steel, etc. In this book, the name "metal" is used in the popular meaning. These have various popular names, which can, due to their application fall under more than one category viz.: heavy metals (Fe, Pb, Cu, Zn, Ni etc.), light metals (Al, Mg, Si, Ti etc.),

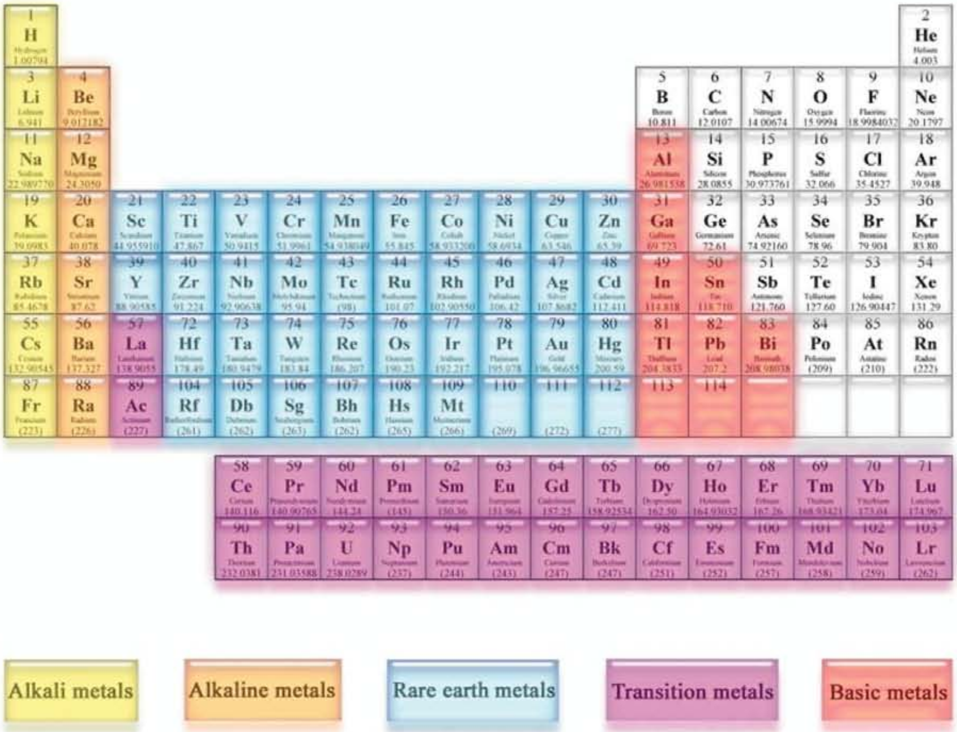

Figure 1.3: Periodic Table of Elements; the shaded parts in represent the different metal groupings

alkali metals (Ca, Na, K, Li etc.), refractory metals (Al, Cr,Ti etc.), steel alloying elements (V, Nb, Mn, Cr, Ni, W etc.) to name but a few. Metals can in theory be reused countless times, with significant savings in energy and reduction of waste compared to primary processing. In this book a number of non-ferrous metals are investigated in the context of sustainability (B). The role of this technological knowledge in the achievement of sustainable metal use, and the provision of the knowledge to stakeholders is the focus of this book. Traditionally, the non-ferrous metals industry has been widely regarded as having a negative environmental image. As a result, the substantial and continuing improvements in the environmental performance of the non-ferrous metals industry have not been generally appreciated. Improved communication between and the provision of comprehensive information to all stakeholders are necessary for the industry's continuing environmental improvements to be recognized, used and steered towards sustainability. The investigation into the "ecology" of metals presented provides an understanding of metallurgical processes as interacting units and of their roles in the resource cycles. On the one hand, this understanding provides a better basis for more sustainable product designs, waste management and development of economics and policy and legislation. On the other hand, it shows the systemic constraints and opportunities for the design and operation of metallurgical processes.

1.1.2 Economics of metal processing and recycling

Metals and metal containing material have intrinsic economic value. The value of pure metals, scrap, ore make the material cycle possible. Without it the ideals of Industrial Ecology cannot be made true. Without going into the depth of the economics of the material cycle, which is included in our optimization models, a few sources are given where the economic value and the production data of various materials and metals can be obtained.

- London Metal Exchange *[www.lme.co.uk]*
- Metal Bulletin *[www.metalbulletin.com]*
- Brook Hunt *[www.brookhunt.com]*
- CRU International Ltd. *[www.crugroup.com]*
- US Geological Survey USGS *[http://minerals.usgs.gov]*

1.2 Societal and scientific relevance

Current waste management in Europe represents an enormous loss of resources both in the form of materials and energy [18]. The problem of minimizing resource losses and the environmentally sound abatement of waste requires rethinking of the function of waste infrastructures. The waste infrastructure, like other public infrastructures, is submitted to many contradictory forces, which were often not accounted for in the design. Traditionally, infrastructure has to deal with the inertia resulting from the sunken cost (related to the high investments in the infrastructure), and from the associated legal framework and administrative organizations involved (see the frame "Development of waste infrastructures" below). For the design of new infrastructures, long technical life spans were assumed and logically also long time horizons for decision-making. The evolution of the socio-economic perception, combined with the influence of new or advanced technologies, however, has shortened the time horizon of decision-making on the infrastructure: The market for public services increasingly becomes more international, this combined with the development towards liberalization and privatization of the utility sectors, stimulates a short-term market-oriented approach. This has many consequences for the regulatory framework and administrative organizations [19]. Particularly considering that, unlike the other public infrastructures, an improved design, operation and management of waste infrastructures can not solve this problem. The objectives for waste management are part of a larger objective, viz. prudent resource management and sustainability. Consequently, adequate design and management of waste infrastructures will require a change in the thinking, concepts and tools.

1.2.1 Development of waste infrastructures

Recyclable materials are generated broadly speaking in the industrial manufacturing chain and in the consumption chain. The former are usually easier to recycle due to their simpler property spectra. The materials discharged in the consumption chain can be divided into the durable goods and into household waste. The former group consists of cars, electronics, household appliances and the like. The book discusses the challenges of this group using end-of life vehicles as an example. The household waste contains organic material, metals, paper, cardboard, plastics, ceramics, wood etc. in varying proportions. These are taken care of by the waste management infrastructures. Public infrastructures are large-scale technological systems that consist of immovable physical facilities, and deliver an essential public or private service through the storage, conversion and/or transport of certain commodities. The (sunken) costs of these infrastructures were so high, and the consequent economic life spans of the infrastructures so long, that neo-classic economists considered them typical examples of natural monopolies. According to them, submitting a natural monopoly to the market forces, would lead to negative effects on the prices or the equal availability of the infrastructure services [20]. This has led to government interference into the public utilities in Europe. The essential service the waste infrastructure delivers, concerns the removal, disposal and recovery of municipal solid wastes (MSW) with minimum harm to public health and the environment. Sound waste management is an integral part of environmental protection [21]. Improper disposal of municipal waste can result in unsanitary conditions, which in turn can lead to pollution of the environment and to diseases. This significance of waste management for public health and the environment has lead to the development of public waste infrastructures. Robust, durable infrastructures have been constructed to safely dispose of the waste generated, and minimize impacts on environment and public health. These infrastructures include waste collection systems, a network of transshipment and separation points, and a limited number of disposal options such as landfilling, incineration and composting. Generally, waste is collected in a multi-stream collection system (Figure 1.4). Each waste stream is transported via various transshipment and/or pre-treatment nodes that have a buffer function also. To a limited extent sorting of waste occurs after collection. The waste infrastructure converts remaining waste into electric power and heat, fertilizer, and ashes usable in e.g. road construction and cement production. One of the typical waste infrastructure characteristics is that it deals with a great many different entities, whereas other infrastructures must only deal with a single principal entity (electricity, natural gas, water, or bytes). "Waste" is really an aggregate term for a large variety of materials. The only common denominator of these materials is the fact that they are discarded after their useful product lives. In order to avoid resource losses, these materials must be recycled (i.e. processed into resources for new products). For many materials, however, the actual recycling process is carried outside the waste infrastructure, viz. in the industrial production processes. In these processes, the wastes often (partially) substitutes virgin or primary materials. It can thus easily be seen that the minimization of resource losses in waste management is directly related to prudent management of resources, one of the cornerstones of sustainability. The focus on safe treatment of a large variety of discarded materials, and minimization of impacts on environment and public health, however, has lead to a development of more or less autonomous waste management policies and to infrastructures that are "sinks" rather than "sources" of raw materials for (the recycling) industry: large amounts of final residues must be landfilled. In addition, the resources recovered are of relative low quality, apart from those obtained from separate collection systems, some scrap metals and electricity.

1.2.2 Support of decision-making

For prudent management of resources, restructuring of current waste management practice and infrastructures is required. From a systemic point of view, the necessity of an integrated resource (production-recycling-disposal) system is obvious. In this view waste is considered as an only "emerging attribute" of a resource. This idea is not an entirely new one, as in many industries some processing of waste becomes economically and ecologically feasible, and the substance or object previously labelled "waste" changes into a "resource"[22]. This perspective also forms the foundation of a movement towards a cyclic economy that resembles the way nature's ecosystems are built up: a network of integrated processes that form cycles. "Industrial ecology" uses this analogy to capture and build upon it a strategy for sustainable development [11, 12, 13, 14, 15]. The concept of resource cycles combines industrial systems and waste infrastructures that generate and assimilate waste [23, 24, 22]: they describe the "life" of a resource from cradle to grave: resource extraction (mining, drilling, etc.), processing in to suitable raw materials, application in products (manufacture), consumption and finally disposal or recycling (Figure 1.5).

The necessary broader scope complicates the decision-making on waste infrastructures. Many problems in operation and management of waste infrastructures require solutions in the downstream and upstream industrial processes. If decisions are made on either the waste management or production infrastructure, the consequences for the resource cycles must be taken into account. From a resource cycle perspective, waste management is an important node that affects the availability and fate of all chemical elements. In product manufacture, many different materials are combined into products. The subsequent discarding of these products generates waste that contains many of the chemical elements (Figure 1.5). Waste management must process and separate these materials so that these meet the capacity and specifications of industrial processes downstream. In other words, where product manufacture couples the resources of materials, waste management must partially decouple these again so that the materials can be effectively recombined into new products. The recycling of steel can be used to illustrate this. The manufacture of a car involves the combination of several materials, including steel, aluminium, copper, zinc, glass and plastics. Dependent on the specifications and capacity of the industrial recycling processes downstream, these must be separated in waste management processes. Steel, aluminium, and copper must be separated before recycling in metallurgical processes. If they are not separated, this can result in large process residues, and/or off-specification secondary metals and alloys (down-cycling), which inhibits the recycling of these metals. Zinc is used in the automobile industry for steel corrosion-protection (zinc galvanizing). Removal of zinc is essential for the resource cycle of zinc, as about half of the total global world production of zinc is used for galvanizing (Figure 1.6). However, zinc need not to be separated in waste processes. The presence of a zinc coating on steel does not restrict its recyclability, and zinc and steel are usually separated in steelmaking processes. Before recycling the metal to the oxysteel-furnaces, the zinc must be

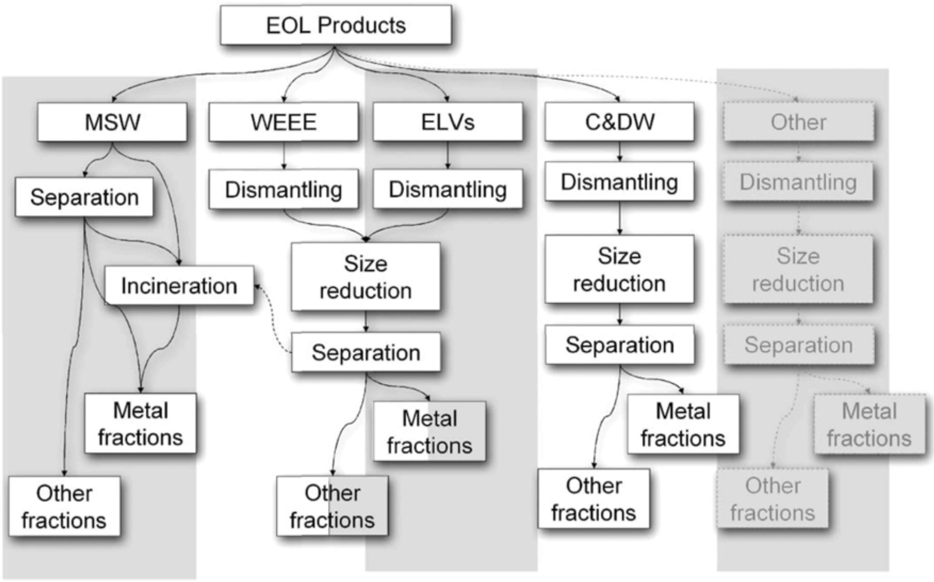

Figure 1.4: Schematic of waste infrastructure

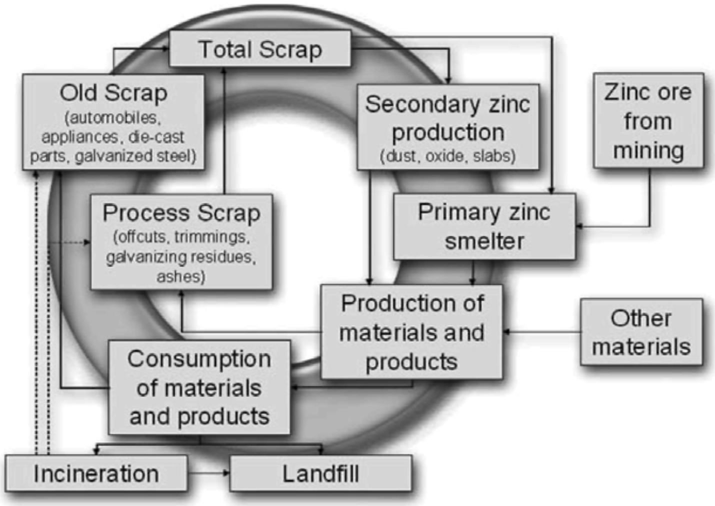

Figure 1.5: Schematic overview of the zinc resource cycle

removed; otherwise it would destroy the furnace. Zinc and steel can be separated before feeding the scrap to the basic-oxygen furnace, for example by electrochemical dezincing systems. However, most of the galvanized steel is recycled in the electric arc furnace (EAF) process. The zinc volatilizes in the process and is collected for reprocessing. Globally, approximately 30% of EAF finds its way to zinc producers and the zinc resource cycle. As a consequence, the infrastructure design problem includes the selection between several pretreatment and separation technology alternatives for each part of a waste management system. The feasibility of the alternatives is dependent on the capacity and specifications of industrial processes. Because decision-making on the use of these alternatives can not be done without considering the resource cycles, this concept offers a convenient method of abstraction to model the broad spectrum of technologies involved. It enables a shift in focus from single linear technologies to interconnected cyclic systems that must realize a prudent management of resources. The concept of resource cycles thus appears a good basis for the new approaches and tools required.

A requirement of these new approaches and tools is that they must connect different "organizational" levels (chemical process design and control , micro-economics, local, regional and (inter)national policy and legislation). The design and management of sustainable waste infrastructures must be a combined effort of decision-makers at various organizational levels both in public bodies and industries, particularly in view of the current developments in the waste sector, such as internationalization, liberalization and privatization. Since process engineers act at a different organizational level than regulators or policy-makers, the approaches and tools must be able to link opportunities and constraints of waste recycling at the level of chemical reactors in the industrial processes to the organizational level of the regulators or policy-makers. Where regulation at governmental level is a control instrument to achieve a certain set of objectives, it is a boundary condition for an industrial decision-maker. The EU directive on the incineration of waste, for example, excludes a number of environmentally sound industrial options for co-incineration. Consequences of regulations must be made

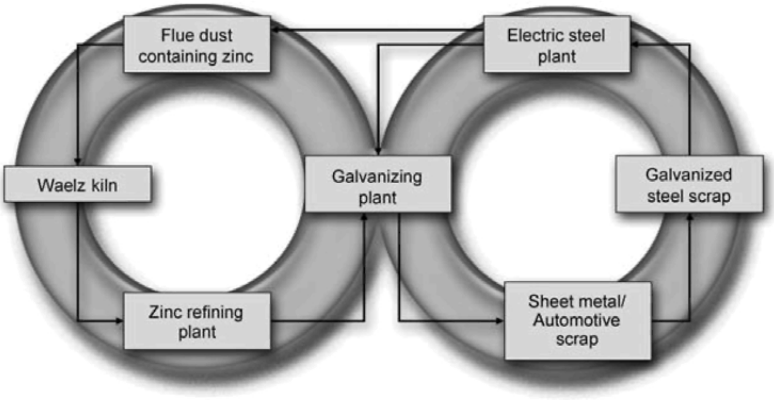

Figure 1.6: Schematic overview of the coupling of zinc and steel resource cycles through galvanizing

transparent by demonstrating how these affect the technological system, and vice versa. Using the interconnected resource cycles as leading concept, tools can be developed that facilitate communication between regulators, decision-makers and system designers and use an understandable logic originating from a solid technological base. Therefore, the flows of metal through society are described from reactor to the global, interconnected metal resource cycles. The consequences of prudent resource management for process design and operation of metallurgical reactors are discussed. The role of the identified metallurgical constraints and opportunities for recycling is analysed with respects to product design, waste infrastructure design and operation, and policies and regulation, which create the economic incentives and boundary conditions that shape the flow patterns of metals through society. Finally, based on this analysis, a model of the interconnected metal resource cycle is presented to support co-ordinated decision-making across the different system levels.

1.2.3 Systems approach

Bertalanffy was among the first to argue problems can not always be understood by analysis alone. Some of the properties of the parts of the investigated systems are not intrinsic properties, but can be understood only within the context of the larger whole [25, 26, 27, 28, 10]. This contextual, or system thinking is the opposite of analytical thinking. Where analysis means taking something apart to understand it, systems thinking means putting it into the context of the whole. The basis of system thinking is that in any system individual parts can be discerned, that these parts are not isolated, and that the nature of the whole system is always different than the sum of its parts [10]. Therefore, the inclusion of sustainability and industrial ecology in this book necessitates a system thinking approach. The study started with a broad and ill-defined problem of an optimum "arrangement of the network of waste processing facilities for metal containing wastes" with respect to sustainability. The determination of an optimum arrangement can not be based on the intrinsic properties of the infrastructure alone and must thus be considered in the context of the global, interconnected resource cycles. The underlying body of knowledge on sustainability and industrial systems thinking (i.e. industrial ecology) is relatively new and still "maturing". This book thus encompasses a relatively large area of research and has started from a relative small body of knowledge. Moreover, as with most systemic studies, the added value or depth lies in the connection between the parts [29].

1.2.4 Motivation for processing of residual material

In the past, recycling efforts have certainly been motivated by the high economic and emotional value of metals, since metals have always been expensive, their production costly and associated with very sophisticated know-how, their properties unique and outstandingly coveted, or their occurrence often extremely scarce. Until now nothing fundamental has changed. In 1972 the Club of Rome published its prophetic book on the "limits of growth". Despite the simplicity of the computer simulation models used at that time one message has been accepted all over the world: Earth is a closed system and our resources, in particular our material resources are limited. About 10 years later most of the key statements have been corroborated by the "Report to the President of the USA" which presented moreover quite a lot of detailed data. These publications served as a steady "push" to reduce emissions, irrespective of being gaseous, liquid or solid. Green movements felt confirmed in their principle scepticism about unchecked, ruthless consumption behaviour and politicians came under ongoing pressure to act. A host of so-called environmental laws, rules and regulations have in the meantime been passed into various national and international legislations. One of the basic motivations - temporarily forgotten in the public - was the preservation of raw material resources. This worked as a driving force for a systematic separation and collection of all kinds of waste, especially in Europe, is predominantly organised by the local communities. Since then metals are collected, now more organised and separated into classes of metals, paper, plastic and batteries, spent solvents, paint sludges, irrespective of its origin. This book is dedicated to the role of recycling as a raw material preservation tool (excluded are energy resources like, coal, wood, natural gas or other fuels), but not deal with environmental aspects in general. No doubt recycling activities fit perfectly under the umbrella of environmental protection, however, not every environmental action automatically helps preserve raw material. The economic incentive for any kind of material trading (also typical for primary and recycling metal production), could be characterised as a "pulling" force, whereas legislative measures serve as a "pushing" force. The former as a typical market effect worked almost perfectly over the last number of millennia, however the latter is an initiative of the last three decades of the twentieth century, sometimes with questionable results.

In summary, therefore, the motivation for the treatment of residual material and recycling is:

- scarcity or shortage of resources *(Example: Regeneration of spent foundry sands; reforming of metallic goods. This includes scarcity or shortage of raw material contained therein; it could be local, domestic etc.)*,
- high monetary value of raw material contained therein e.g. by high content [wt.%] or/and high price [Euro/weight unit of corresponding material] *(Example: Recycling of metal scrap for used beverage cans (UBC), transformers, recycling of precious metal containing products, such as catalysts, photo films, regeneration of special lubricants etc.)*,
- potential hazard of material e.g. Hg, Cd, As, radioactive material, poly-halogenated hydrocarbons *(Example: Vitrification of spent nuclear material, delaboration of spent*

ammunition and explosives, destruction of ABC weapons, materials in transformers etc.) are treated by:

  - thermal or chemical destruction
  - inertization or immobilization (e.g. vitrification) at high temperature
    underground disposal
  - secured disposal pond

- low bulk density [t/m^3] of residual material which effects its necessary transportation *(Example: Crushing of glass bottles; shredding of aluminium cans, compacting of scrap in to bales, compressing foamed plastic, etc.)*, and

- high heat value of residual material which is attractive for replacement of natural fuels *(Example: Incineration of mixed plastic, incineration of organic solvents etc.)*

Note: Processing of residual material can clearly be defined as recycling, as long as material is fed back into industrial cycles. In all other cases when no material is returned back into industrial cycles, one speaks of treatment.

1.2.5 System approach to car recycling

Modern society is characterised by the extensive use of complex multi-component consumer products, of which passenger vehicles are a typical example. These modern consumer goods and products are manufactured by using a wide spectrum of different raw materials to meet highest consumer, safety and environmental requirements. Moreover the construction and manufacturing of these goods and products should be carried out in an energy efficient and environmentally friendly way. The products themselves and their use or operation should also contribute to the overall sustainability, e.g. by applying light weight materials in cars to reduce energy consumption during use. At the end of their useful lives these products will be discarded and return as complex multi-component materials that cannot directly be converted into products once more. At this moment 8 to 9 million tonne waste originating from end-of-life vehicles is coming free per year in the EU Community [30]. Society requires that a maximum percentage of materials and/or energy coming from these end-of-life products find their way back into the industrial and consumer resource cycle to ensure a sustainable development of our society. The European Union directive on the recycling of passenger vehicles [9], imposes strict recovery and recycling targets to be achieved in the nearby future. Moreover, calculations to predict the recyclability of the car are required for the proposed directive for the type-approval of cars [31], which have to obey to the targets as laid down in the EU directive on passenger vehicles [9]. These strict recycling targets are one of the driving forces for more awareness on the importance of recycling in the product's life cycle as well as for the optimization of recycling systems. Placing Car Recycling within the perspective of Figure 1.1, the following philosophy of car recycling can be presented.

Technology Cycle

The basis to describe and understand recycling systems is the combination of recycling technology (Technology cycle in Figure 1.1) and the material flows (Resource cycle in Figure 1.1) within this recycling system being represented by the recycling flowsheet for a specific product or material. Simply stated, car recycling consists of a combination of various processes ranging from de-pollution and dismantling, shredding and physical separation, to metallurgy

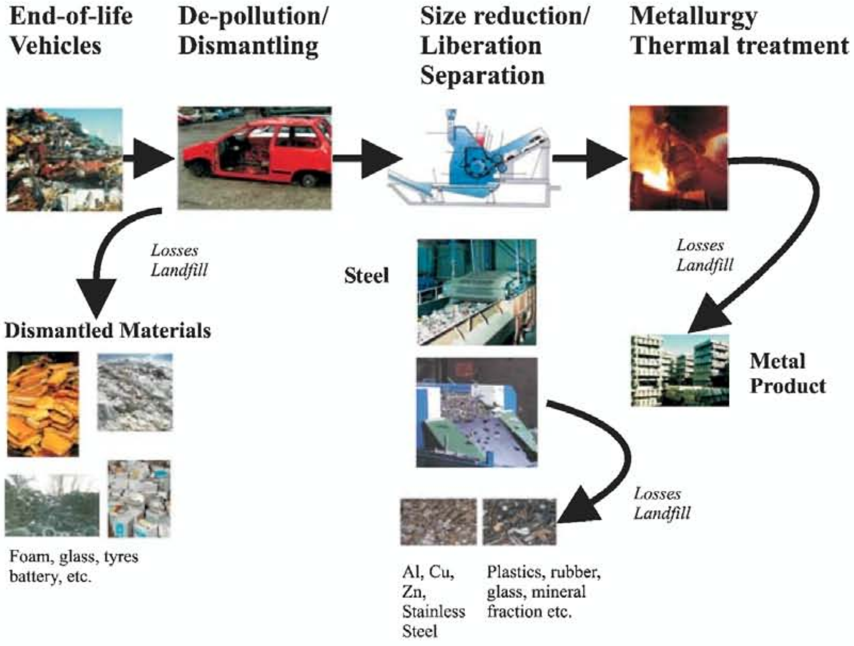

Figure 1.7: Simplified flow sheet of recycling passenger vehicles - design affects all losses

and the processing of (in-) organic components, in combination with thermal treatment of recycling (intermediate) products for energy recovery (see Figure 1.7). Even incineration and land filling can be part of the end-of-life scenarios, although land filling and incineration without material or energy recovery are not considered as recycling according to legislation [9] (Life cycle in Figure 1.1), but are however fundamental to include in the recycling flowsheet in order to determine and control losses in the system.

Each of these separation and processing steps (except for incineration and land fill) contributes to the recycling and recovery of the various materials composing the car, either by producing a product stream or an intermediate recycling stream, which will be the feed to subsequent separation or recovery processes. This reveals the inseparable relation between the different processes and material flows in the recycling chain of end-of-life vehicles. The product quality, particle size, and composition of the input for e.g. to metallurgical processing are determined by its preceding processes, such as dismantling, shredding (size reduction and liberation), and mechanical separation. The design of the product plays a significant role in this recycling chain. The materials used, as defined in the design of the car, will differ in their specific recovery rate an their material combinations. This will in turn affect the quality of the (intermediate) recycling products and therefore the recycling rate of the car. The separation of materials by each of the process steps in the recycling chain will inevitably lead to loss of materials. Due to the interrelation between grade (quality and recovery of mechanical separation processes (which implies that both high recovery and grade requirements cannot be fulfilled at the same time) [32] the recovery of materials will always be lower than 100%, if the quality of recycled materials has to be increased by mechanical separation. A high quality feed to metal producing processes is of critical importance to ensure the economic production of high quality metal products after (s)melting, which is indispensable in achieving high recycling rates [33]. As an example the metallurgical processing of the ferrous fraction coming from end-of-life vehicles illustrates the importance of being capable to produce a high quality recycling (intermediate) stream by the combination of dismantling and mechanical separation processes. The maximum concentration of Cu present in the ferrous stream is restricted to 0.25%. Copper cannot be removed from the melt because of the similar chemical activities of Cu and Fe. Too high copper content will change the structure of steel prohibiting its general use. As an other example, the recovery of aluminium is dependent on the purity of the input stream of the metallurgical process, created during mechanical recycling of, in this case, the car. High contents of e.g. Cu and Fe require that primary metal be added to achieve the required alloy composition after melting. The increasing product complexity and changing material combinations in the design cause further losses within the recycling phase. For example, the mechanical separation of complex materials (e.g. the separation of aluminium from organics combined in Al-laminates) to produce material streams with the desired specifications for further processing, will not always be possible from a technological or economical point of view. The increasing complexity of the design of the car, as well as the application of lightweight metals (aluminium, magnesium, etc.), plastics and even composite materials will complicate the recycling of passenger vehicles even further. There is an inseparable relation between the different processes and material flows in the recycling chain of end-of-life vehicles and the designs applied to produce new cars. In view of EU legislation it is required for the automotive industry to be able to calculate and predict the recycling rate in the design stage of the car. Moreover optimization of recycling, in close connection to design for recycling, is essential in order to realise the recycling targets as imposed by EU legislation (Life cycle, Figure 1.1).

Resource Cycle

The use and general understanding of the term *primary* and *secondary* raw materials within the Resource Cycle, as well as subsequent terms such as *primary* or *secondary* metallurgical processes needs clarification. There is a good reason for this: In the recent past the commonly used word "secondary" was often mistakenly taken as a reference to the quality of the material, which was seen as "second best" i.e. of lower quality, lower reliability, lower stability, lower durability, lower firmness, etc. Consequently the consumers believe that products manufactured from such secondary material are of "second best" quality and prefer products made out of primary material, although, due to modern standards and quality control there is in principle no difference between products manufactured from primary or secondary material. The word *primary* indicates that such material enters the production and consumption cycle for the *first* time. The expression *secondary* is used to indicate that a material has entered the industrial cycle at minimum for the *second or more* time. After two decades of fruitlessly fighting the instinctive public interpretation of "secondary" it is felt that a new term is needed, since marketing products made out of so-called *secondary* material is severely impeded. For example, in their brochures European automobile manufacturers eagerly point out small gadgets made from "recycled" plastic. However, they hardly dare to mention that numerous metallic components in their impressive cars are, and have been for some time, produced from secondary raw material (scrap), including the technically highly advanced engines made from aluminium alloy scrap. The term *primary* is neither a misleading nor an inappropriate expression of what is meant, wherefore it is retained in this book. Due to the instinctive misinterpretation of the term *secondary* raw material should be replaced by *second generation SG* raw material. According to the tendency of applying acronyms one may use

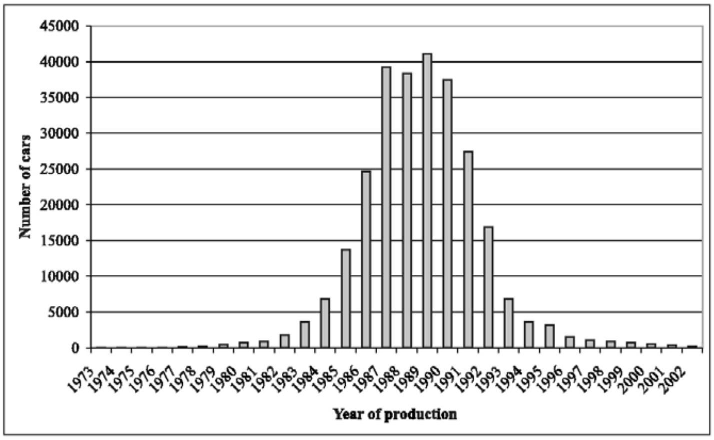

Figure 1.8: Number of end-of-life vehicles discarded in the year 2003 as a function of the year of production [34]

SG raw materials. The material and energy flows within the resource cycle of the car (Figure 1.1) are determined by the design and recycling of the car (Technology cycle, Figure 1.1). In the design of the car various materials are combined and connected in many complex different ways, making up the complex composition or "mineralogy" of the car and its components, which is changing rapidly and continuously over time. The total volume of cars produced each year consists of many different types of cars, of which each will have a different degree of recyclability due to their specific weight and composition. Furthermore, the lifetime of the car will also differ individually over time for the various types of cars. As an example, Figure 1.8 shows the number of end-of-life vehicles discarded in the Netherlands in the year 2003, which originate from a range of production years. Figure 1.8 shows that the life time of the car cannot be represented by an average value, but is a distributed and can therefore only be captured by an average value in combination with the standard deviation around it.

Figure 1.9 shows the diverse (and distributed) population of end-of-life vehicles in at a certain moment in time collected at a shredder site, whereas Figure 1.10 gives the distribution of the weight for these vehicles. Figure 1.8 to Figure 1.10 clearly illustrate the statistically distributed nature of recycling end-of-life vehicles and make clear that the life time, weight and composition of the car can only be described by a distribution.

The average weight per vehicle and (dismantling) year is the basis for the calculation of the recycling rate as well as the definition of the recycling rate as imposed by the EU directive on the recycling of passenger vehicles [9] (see Eq. 1.1) and represents the distributed weight and material use in the car at the time of production, coming back for recycling in a certain dismantling year according to the life time distributions of these cars.

$$\text{Recycling Rate} = \frac{\text{average wt. of recycled/recovered material per vehicle per year}}{\text{average wt. per vehicle and year}} \cdot 100\% \tag{1.1}$$

From the above it would be evident that the dynamic material and energy flows of the resource cycle system are a function of the various involved statistically distributed and time varying parameters such as the life time, weight and composition of the car, of which the

Figure 1.9: Diverse and distributed nature of the population of end-of-life vehicles in the Netherlands (2003) and an example of the grade of its recycling (intermediate) products

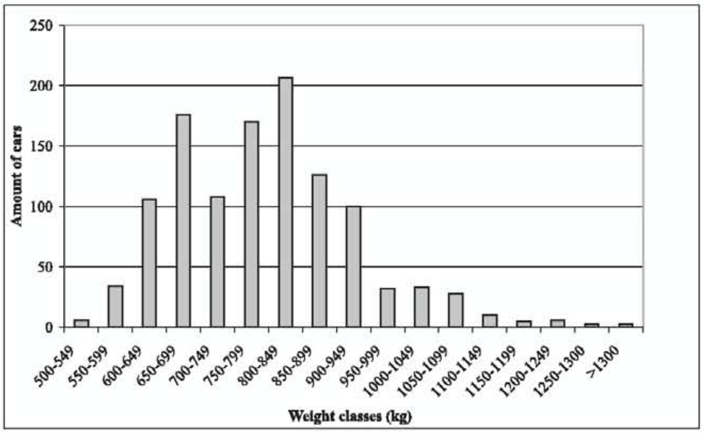

Figure 1.10: Weight distribution of end-of-life vehicles of the population of end-of-life vehicles in the Netherlands in 2003 of 1153 cars [35]

combination determines the input of the recycling system (average weight and composition of the ELV population) on a certain moment in time. This implies however, that the recovery of the various materials in the car and hence the recycling rate, which are determined by the dynamic and distributed parameters within the resource cycle, is also a dynamic and statistically distributed value. The statistics around the parameters determining the recycling rate indicate that the (calculations for the) recycling rate and requirements for type-approval of cars as imposed by legislation in Europe should also be based on a statistical basis and are meaningless if represented by a single value. The dynamics of any recycling system and therefore the recycling rate are defined and described by these distributions. The reality of car design and car recycling cannot be presented without a statistical framework. Failing to realise this will lead to erroneous definitions for recycling to be formulated. The dynamics of any recycling system and therefore the recycling rate are defined and described by these distributions. The International Organization for Standardization [36] has developed a calculation method for the recyclability and recoverability of cars. Static treatise, like the ISO norm, will lead to erroneous definitions for recycling to be formulated. Only a statistical treatise can supply the designer with information on the relation between the design, the recovery of materials from the car, as well as the quality of recycling products determining ultimately the recycling rate.

Life Cycle

In view of EU legislation imposing strict targets for the recycling [9] and type-approval of passenger vehicles [31] recycling is becoming an important aspect in the design of the car. It is essential that the recycling rate can be calculated and predicted in the design phase. Moreover, due to the rapidly changing and multi-material new lightweight design of the car, in which the use of lightweight materials is steadily increasing, recycling is complicated and has to be optimised in order to be able to comply with EU legislation on recycling and type-approval. The link between design software tools and recycling models has still to be established on a solid technological and fundamental basis in order to predict the recyclability of the car during the design phase, as well as to be able to apply design for recycling and is therefore up to now a much misused word. In existing literature the recycling of the car is simply described by referring to the different processes and materials involved in the recycling of end-of-life vehicles [37, 38]. In most of these studies recycling is regarded as a combination of de-pollution, selective dismantling and physical separation steps, in which the crucial role of metallurgy is often neglected. Discussions on (car) recycling are also presented in literature within a broader philosophy such as Industrial Ecology [39, 40] , MFA studies [41], studies on sustainable development, and Design for Environment (DfE) strategies etc. [39] and [42]. In these works recycling is described as one of the parameters in the larger life cycle system, which is obviously the case as discussed above. Moreover recycling is discussed in view of Design for Recycling (DfR) strategies [40, 43, 44, 45]. However in these studies, recycling is in general presented in a far too simplified manner, in which detailed technological knowledge, which is required to capture the complex interaction of processes and material and energy flows within the interconnected recycling system is lacking. The crucial role of the quality of recycling (intermediate) products in the realisation of high recycling rates as well as the role of product design and its complex interaction with the recycling of end-of-life vehicles is not addressed. This implies that recycling cannot be optimised something that is often suggested in these studies without a fundamental basis. Design for recycling can never be realised, when the technological framework of recycling is represented in a too simplified manner and will therefore only result in very general and trivial guidelines. No studies were found, which combines a systems approach of the resource cycle with that of recycling, based on a detailed technological knowledge of the complex, statistical and dynamic interactions of recycling systems in relation to the design of the product underpinning in a fundamental manner legislation. The authors also have been involved in life cycle assessment studies for cars [46].

1.2.6 System approach to the recycling of aluminium

Aluminium is hardly used as unalloyed metal. Its use as one of the leading non-ferrous metal is dominated by the excellent properties of its various alloys. There are two categories of aluminium alloys: Wrought alloys, low in Si, used for rolling and extrusion, and cast alloys, high in Si, used for casting. Typical products from wrought alloys are sheet, packaging foils or window-profiles. Those from cast alloys are engine blocks for automobile or gearboxes. Aluminium alloys are to a certain degree self-protecting against atmospheric corrosion by forming an oxide layer on its surface when in contact with air or water. Such corrosion resistant layers could also be electro-chemically generated and coloured simultaneously. Together with the low density of 2.7 t/m^3 the physical properties of aluminium alloys led to a very specific end-use pattern of the 8.4 million tons of aluminium consumed in Europe in the year 2001, as shown in Table 1.2.

Table 1.2: End-use pattern of aluminium in Europe for 2001

transport	32%
building	26%
packaging	19%
engineering	14%
other applications	9%

In 1888 the world production - in this case equivalent to consumption - of aluminium was 2 t/y, 115 years later the consumption reached 25 million t/y. This means that the consumption of aluminium increased by a steady growth rate of 15%/year during the last 100 years. No other metal shows a similar growth rate. The recycling of aluminium commenced rather early: As early as 1916 the first secondary smelter started its operation in the USA followed by a smelter in Germany in 1917. Since then aluminium has been increasingly remelted, prevailingly as "Duralumin", however, after 1945 numerous new aluminium alloys have been developed and consequently remelting has become a more and more difficult operation. At present in Western Europe there are about 170 aluminium refiners, which convert collected old aluminium scrap to standardized alloys. The two alloy categories "wrought" and "cast", the fabrication processes and its specific losses, its typical end-use pattern and the specific lifetime of the various goods and articles determine the aluminium cycle. The consumption of aluminium in the transportation sector is dominated by the automobile sector. Whereas in 1990 about 50 kg of aluminium alloys were used per passenger vehicle, this figure increased in 2001 to about 110 kg. In average after 12 to 14 years the aluminium from old cars will return as a result of the car recycling endeavours in Europe. Approximately 65% of all cars built in a given year will be returned to the organized European car recycling system; the difference disappears to eastern European countries or Asia. A very first assessment of the aluminium inventory in European buildings (residential and non-residential) resulted in a stock of presumably 30 million tons of predominantly wrought alloys. This aluminium will first return after 30 to 70 years, when buildings are scheduled to be demolished. However, the average lifetime of aluminium windows, due to more insulated-glass related constraints, is about 27 years; this could result in an earlier return of significant tonnages of aluminium from buildings prior to their demolition. Packaging aluminium will return to the re-use cycle much earlier: Foils or used beverage cans may resurface after a couple of days or weeks. The average lifetime of goods - passenger cars as well as used beverage cans - is easy to misinterpret. For example passenger cars of a given construction year will be de-registered according to a distribution function. The first car may be shredded after a couple of days, others will be driven over 30 years. The average car lifetime of 13 years simply says, that in the year 2003 50% of all cars from the construction year 1990 have already been de-registered and presumably dismantled and/or shredded, the other 50% still being on the roads, however, this is a simplistic view that will be discussed in much more detail in II. The losses when collecting aluminium alloys after the end-of-life of goods and melting the collected scrap are quite high. Of the 8.9 million tons of aluminium fed into the European aluminium production and fabrication industry in 2001, about 3.0 million tons of aluminium originated from scrap. Using an average lifetime of all goods manufactured from aluminium alloys of 12 years, and a moderate growth rate of aluminium consumption in Europe of 3.5%/y, the present consumption figure of 8.4 million tons of aluminium alloys (2003) result in a consumption 12 years ago of 5.6 million tons of aluminium alloys in Europe. Compared with the 3.0 million tons of scrap available 12 years later, the total losses sum up to about 2.6 million tons; the recycling rate would be about 54%.

The aluminium cycle in Europe is at present characterised by a demand of about 8.4 million tons of aluminium alloys and an impressive volume of continuous returning tons of various aluminium alloy scrap from relatively small sectors. The substantial losses do, however, require an ongoing feed into this aluminium cycle from outside. In 2001 Europe produced about 3.8 million tons of primary aluminium and imported yet another 2.1 million tons of primary aluminium. These 5.9 million tons could be considered as the necessary compensation for the total losses of the aluminium cycle. Regardless of the exact figure it becomes evident that Europe needs a large tonnages of primary aluminium to compensate for the ever-increasing demand and to balance out the cycle losses. Compensating for losses is required even if the growth rate for aluminium consumption in Europe is zero. Similar numbers can be calculated for other economic regions as well. Recycling of aluminium alloys is a must, but primary aluminium metal production is necessary to compensate for the inevitable cycle losses. Moreover, cast alloy recyclers need primary aluminium metal or wrought alloys to dilute exceeding contents of troubling elements, which cannot be removed by refining. Figure 1.11 is based on data published by EAA for the year 2000, depicting the aluminium flow stemming from the three main sources in Europe: Primary, scrap and imports.

Figure 1.11 is useful to understand the consumption streams of aluminium in Europe as an example. About 38% of the aluminium delivered to the market is rolled material, 30% is extruded (total wrought 68 %) and 26% is cast material. The remaining 6% are special formats, like aluminium powder and shot metal, and in particular metal for steel deoxidation (about 300 000 t/y). More significant is the conclusion that in Europe 5.9 million tons of primary aluminium was fed into the cycle together with 3.1 million tons of scrap originating from on average more than 10 years ago. The recycling of scrap introduces 1.06 million tons of wrought alloys into the primary driven aluminium sectors, whereas the scrap recycling absorbs just 0.4 million t of primary and low alloyed aluminium. This diagram suggests a static linear system: Metal is produced and consumed by the market Figure 1.12. In reality old scrap from markets return i.e. aluminium is circulating. The dynamic system of production, usage, return, re-melting and so forth is called the utilization cycle, which may be found on the supplied CD rom as a dynamic model in Matlab's Simulink.

The aluminium utilization cycle contains all features of a typical complex system: It is

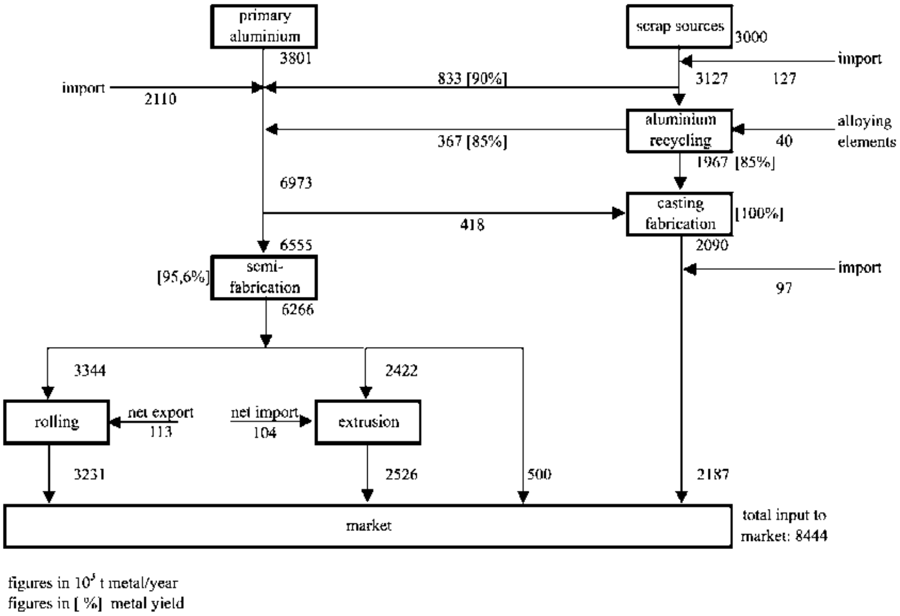

Figure 1.11: Aluminium flow from primary, scrap and imports in Europe

difficult to predict what happens if conditions of the total cycle change. The aluminium cycle is in reality two interconnected cycles: The wrought and the cast aluminium alloy cycle. Figure 1.12 depicts the two cycles and their inter-connection, although it should be mentioned it is a very simplified picture of the numerous flows of aluminium alloy metal containing materials. Moreover it is a steady state diagram, i.e. the time between market in and market out is implicitly set to zero. Nonetheless, it portrays the main features of the system. Primary metal is alloyed to wrought alloys. These are fed to semi-production, i.e. sheet and foil are rolled out of slabs and profiles are extruded from billets. Prompt scrap from semi-fabrication is processed by remelters, which return the metal content back to semi-fabrication. Part of the prompt wrought scrap, however, is offered to the general aluminium scrap market, i.e. it will eventually end up at the scrap yards of refiners. The semi-fabricated goods are machined and combined with foreign material (e.g. other metals and plastic) and eventually delivered to the customers (market). After the end of its lifetime the aluminium manufactured goods are partly collected and fed to scrap collectors. From there the wrought old scrap is transported to scrap processors, where it is up-graded by sorting out unwanted components. The processed wrought old, collected scrap is delivered to refiner plants for melting. Refiners customarily produce cast alloys that are delivered to foundries. The melting produces also some high metal content dross. Refiners eventually melt all dross under salt, including dross from primary alloying and remelter operations. Refiners customarily produce cast alloys that are delivered to foundry plants. There the metal is transformed into final goods, machined and combined with foreign materials prior to being offered to the market. Turnings are returned to the refiner. After the end of their lifetime the cast aluminium manufactured goods are partly collected and handled in a similar fashion to the collected old wrought scrap. Aluminium is a good example of what happens if systemic approach with an understanding of the different

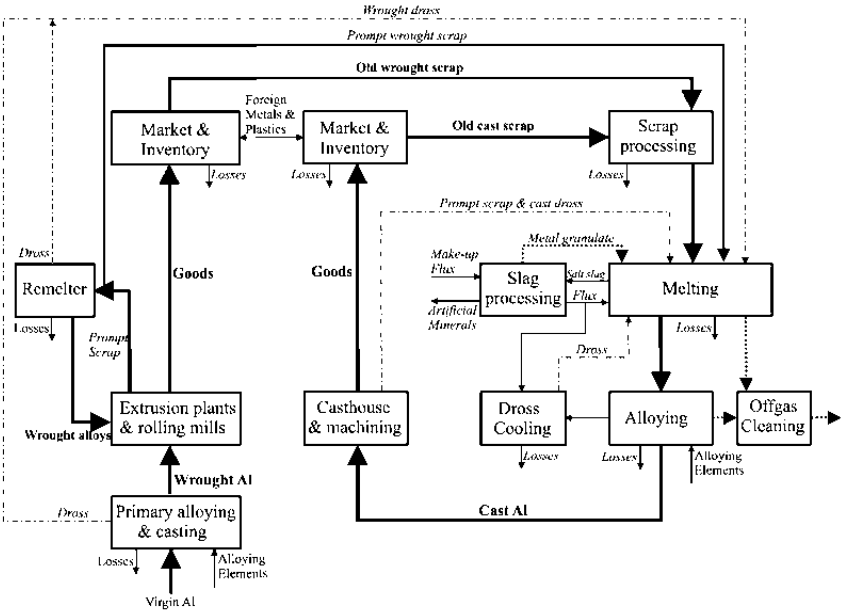

Figure 1.12: Simplified aluminium alloy recycling system - a systemic view

boundary conditions is not applied. Wrought and cast aluminium cycles are only partially interconnected because of such boundary conditions as discussed in Part IV. Production of wrought qualities from a mixed scrap would include the removal of Si from the melt. The oxidation of Si would cause also oxidation of Al. The end result would be a dramatic increase of Al losses in the form of Al-oxides.

Cadre 1.1
The aluminium recycling system in numbers

Figure 1.12 is used to study the system behaviour, with the following given base case scenario data providing some feel for the system:

- *A starting tonnage of e.g. 1000 t of primary metal is kept constant.*
- *Dross is generated at rates of 2-4% of metal input, depending upon the type of furnace used; the metal content of the dross is kept constant at 65%.*
- *According to data received from EAA [47] in average 62% of all semi-fabricated metal input is delivered as goods, i.e. 38% is returned to remelters.*
- *It is assumed that 30% of the 38% prompt wrought scrap is delivered to refiners and 70% is remelted and returned to semi-fabrication.*
- *For the sake of simplicity aluminium alloys are considered to contain just two elements, Al and Si; a first detailed model calculation considered 5 alloying elements with significantly increased complexity but much less transparency.*
- *The wrought alloy shall contain 0.5 wt.% Si.*
- *The refiner must always produce cast alloy with 10 wt.% Si, i.e. usually Si has to be added for composition adjustment.*
- *All final goods to market are contaminated by a 5% foreign metal addition, calculated as Si.*
- *During usage the aluminium alloy fraction of the goods is oxidized; the oxidation during usage generates old wrought scrap with 95% and old cast scrap with 89% metal content respectively.*
- *Scrap processing up-grades the aluminium scrap by separating 80% of the foreign metal (calculated as Si) but generating a loss of aluminium alloy of the same mass.*
- *The refiner operation is calculated by a careful mass balance considering all material streams depicted in the flow-diagram, including the internal recycling of dross from holding furnaces.*
- *The end-of-life collection rate of wrought and cast goods is 70%.*
- *20% of the prompt cast scrap are fed directly to the refiner, 80% are fabricated to goods.*
- *The values for many other parameters were stipulated according to practical experience (e.g. as described in Chapters 13.2 and 14).*

Table 1.3 lists particularly interesting data after running the system model, such as resulting tons of cast alloy production/t primary metal, kg accumulated NMC/t primary metal to be rejected from the cycle via salt flux, and the addition of silicon to adjust the target content of 10% Si in produced cast. These parameters are used to study the system behaviour while changing a few of the above listed variables, the absolute value of which is in fact unknown:

- *collection rate of old wrought scrap,*
- *collection rate of old cast scrap,*
- *percentage of prompt wrought scrap delivered directly to refiners, and*
- *percentage of prompt cast scrap directly delivered to refiners.*

Table 1.3: Effect of some variables on critical Al-cycle parameters

	t cast alloy produced/t primary metal	kg NMC rejected/t primary metal	% Si added to molten cast metal
% prompt wrought scrap to refiner:			
10	1.89	208	2.63
30	1.98	210	2.67
50	2.06	212	2.70
75	2.14	213	2.74
90	2.19	215	2.75
% prompt cast scrap to refiner:			
10	1.81	195	2.91
20	1.98	210	2.67
50	2.75	271	1.96
75	6.07	378	1.38
% collection rate of old wrought scrap			
90	2.40	252	2.66
70	1.98	210	2.67
50	1.56	166	2.70
10	0.72	80	2.84
% collection rate of old cast scrap			
90	3.14	305	1.34
70	1.98	210	2.67
50	1.45	166	4.03
10	0.94	125	6.84

With the assumptions of the base case scenario (bold figures) it is surprising that almost 2 ton of cast alloys per ton primary metal are kept within the utilization cycle. Applying this figure to the momentary primary consumption in Europe of 5.9 million tons/year it becomes immediately evident, that the base case assumptions are far away from reality. The 5.9 million t/a would induce a constant cast cycle of about 11.7 million t/a, which in fact is just about 2.2 *million t/a. The model, however, makes it possible to define a set of assumptions that would produce approximately 0.37 t produced cast alloy/t primary metal, which corresponds with the momentary ratio in Europe:*

- *20 instead of 30% prompt wrought scrap to refiners,*
- *10 instead of 20% prompt cast scrap to refiners, and*
- *20 instead of 70% collection rate for wrought and cast scrap.*

Entering these data into the model it can be established that about 160 kg NMC/t of produced cast alloys should be released from the cycle via salt flux; the actual figure is about 0.4 million t NMC/ 2.2 million t cast production = 180 kg NMC/t, which is in the same order of magnitude. Moreover this set of data requires that the refiner add 7.4 wt.% Si to the produced metal to adjust to the requested target content of 10%; actual figures used at refiners are about 7-9% addition of alloying elements (preponderantly Si) in total, again the same order of magnitude. It would be highly speculative to conclude that only 20% of all goods manufactured from aluminium alloys are collected - nonetheless, a sizeable fraction of the aluminium consumed is used to build up an inventory, like the presumable 30 million tons of aluminium inventory in buildings. [48] The data from Table 1.3 permit the visualization of the effect on the complete recycling system, if some of the unknown variables are changed. In particular it can be seen that the percentage of prompt cast scrap that is directly fed to the refiners has a significant effect on the cycle, whereas the system is almost insensitive to the percentage of prompt wrought scrap that is directed to the refiners; this is a bit unexpected and deserves further consideration.

1.3 The system for recycling of products and metals

The above introduction provides a brief overview of the system engineering approach that will be used to solve various Industrial Ecological challenges in this book. It is argued that this is the only basis on which Metal and Material Ecology can be approached. This provides the basis to define the theory of recycling systems on the basis of a population balance approach (see Appendix A.1.2) incorporating statistics (see [49]) and subsequently moving to the depth of metallurgical processing of materials, illustrated in this book by the theory of car recycling and the metallurgical processing of aluminium. Figure 1.13 depicts these time dependent interactions between product design, end-of-life product, physical separation, metallurgy and thermal treatment i.e. the complete recycling system. Figure 1.14 summarizes the outlook for the future in more detail. It shows how a dynamic model (discussed in Part II and Part III) is linked to an optimization model (discussed in Part III), allowing to predicts the quality (grade) of all material streams as a function of product design, in order to minimize the material losses among others in metallurgy (discussed in Part IV). Predicting the grade is of crucial importance since this determines the value of material streams and whether these can be economically recycled or not. This is also of crucial importance for the prediction of the required recycling rates dictated by law . This book will colour in Figure 1.14 in detail keeping in mind the philosophy of Metal and Material Ecology as depicted by Figure 1.1, but also the fundamental theory developed in this book in addition to the application of well-established theory as summarized and applied in Appendix A.

This book will discuss the tools, theory and models that are required to create the system model for the Design for Recycling and Environment as depicted by Figure 1.14, which include:

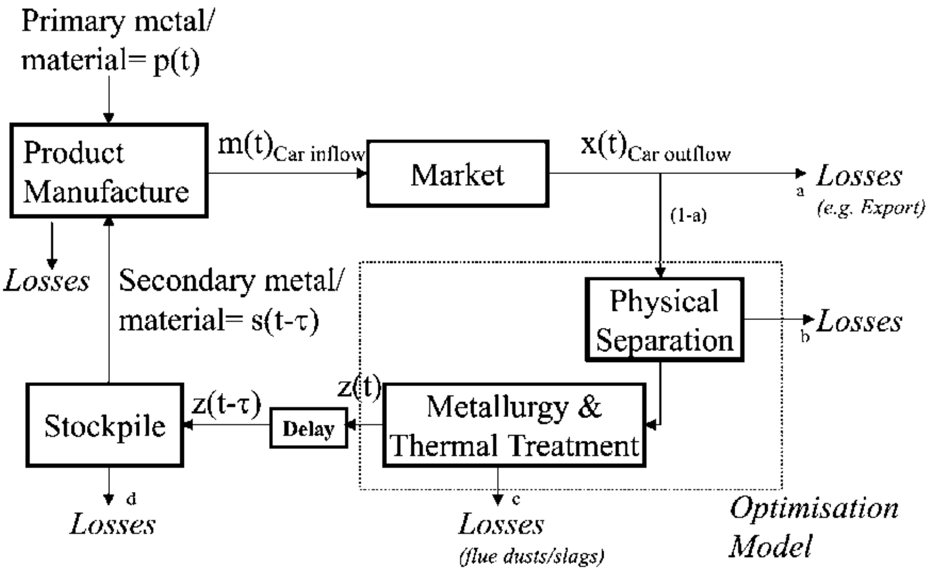

Figure 1.13: The interacting cycles of Figure 1.1 linked in a dynamic feedback loop

- industrial ecology,
- technology, engineering, market and economical aspects,
- environmental legislation,
- system engineering, process control and optimization,
- population Balance Modelling ,
- thermodynamics, fluid flow and the separation physics,
- industrial knowledge/expertise and statistical valid data, and
- system and reactor modelling/simulation.

1.4 Overview of Book

This introductory **Part I** provides a brief summary of the objectives of the three main sections of the book. The previous three introductory chapters gave the reader a brief overview of the three main sections of the book, which will be covered in more depth in each of the **Parts II to IV**:

- **Metal and Material Ecology** - This provides the more holistic philosophical overview and systems approach that forms *the umbrella* of this book.

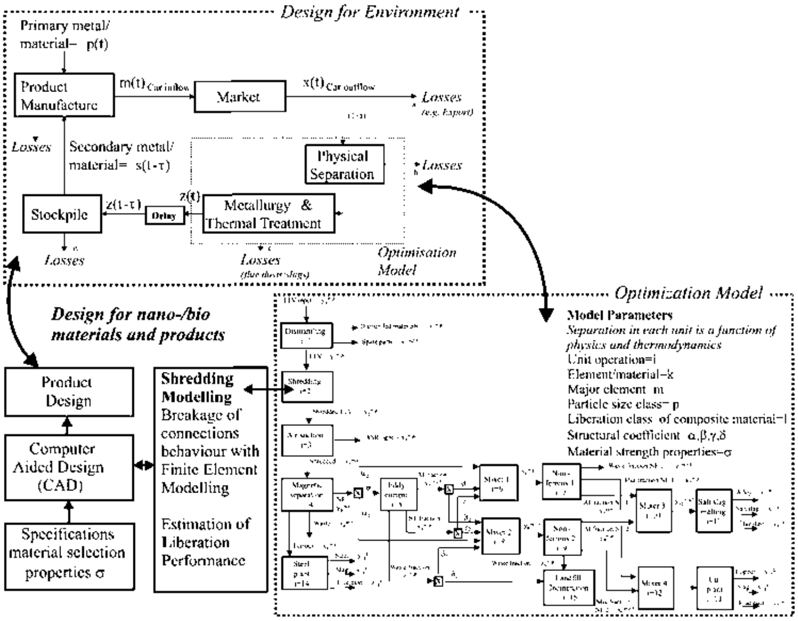

Figure 1.14: A system model that links various dynamic cycles in order to quantify the Metal and Material Ecological System

- **Product Recycling as applied to the Car** - An example how the systems approach links down to the physics, population balance distributed nature and chemistry of the process within the recycling and metallurgical industries *i.e. the spokes of the umbrella*; discussing in addition the link to consumer product design and consumer product producer

- **Metallurgical Recycling of Aluminium** - Indicating that if the fundamentals of recycling technology are not understood well both from an industrial and theoretical point of view, the systems approach has really no value and no foundation to rest on *i.e. the stem of the umbrella*

These sections on will guide the reader from the system of recycling, to car recycling and then to the depth of recycling metallurgy in order to illustrate what depth is required to calculate the various important metrics required to capture the efficiency of the Industrial Ecological system. The reader is referred to Parts II to IV for a detailed discussion and is at all times referred to Figure 1.1 to pin-point at which position she or he are on this sphere at various parts of the text.

1.4.1 Metal and Material Ecology

The problems associated with metal production and use are not intrinsic properties of metals or metal processes, but can be understood only within the context of the larger whole, the metal and material ecology. Similar to natural systems, the metal ecology is a dynamic system: its components and the relationships between them continuously evolve. The development of viable solutions to these problems must thus start with an understanding of the dynamic behaviour of the organisms, the industrial processes. In the end the processes have to realize many of the industrial ecology strategies towards sustainability. Advancing towards sustainability thus must involve the design and management of these processes and development of their functional interactions. Because the process of process and product design; and management spans various organizational levels, it requires co-ordination of stakeholders across all these levels to approach a more sustainable metal production, use and recycling systems. Therefore, in this book it is investigated to what extent improved communication and the provision of comprehensive information to all stakeholders can lead to co-ordinated decision-making. This is then a basis for the development of a resource cycle model to support decision-making on resource management. The central questions of this book with reference to Metal and Material Ecology are thus:

- To what extent does technological knowledge contribute to realization of sustainability or industrial ecology?

- Can tools be developed that assist in the dissemination of the knowledge to the stakeholders?

One of the ultimate goals of this book is to test this hypothesis based on a case study on the metal cycles. To this end, different sub-questions were formulated. In order to answer the central research question, one needs to understand and define the concept of sustainability. Second one needs to understand the role of technology in the achievement of sustainability. Tempelman [29] showed that the role of technology in achieving sustainability is very ambivalent. Depending on how technology is used, it can either be part of the problem or solution. It is therefore essential to take a critical attitude towards technology. Industrial ecology puts technological development into the context of sustainability. As such industrial ecology appears a good analytic framework to investigate the role of technology and technological knowledge. This leads to the following sub-question:

- What are "sustainability" and "industrial ecology"?

Using the concept and toolbox of industrial ecology, the potential role of technology and technological knowledge in advancing to sustainable metal production and recycling systems is further investigated in two steps:

- Is dissemination of technological knowledge a bottleneck for sustainability?
- What is the role of models to co-ordinate decision-making?
- How are recycling and product design connected in the framework of "industrial ecology"?

Finally, it is investigated whether industrial ecology models can provide the necessary knowledge to support decision-making of metal resource management, based on the current status-quo of the models and available data on system.

- Can industrial ecology models provide the technological knowledge?

This is then a basis for the development of a resource cycle model to support decision-making on resource management. Although advances towards sustainability must include all material cycles, not all material cycles, or even all metal cycles can be considered in this book. Therefore, this book was limited to the interconnected metal cycles of a number of non-ferrous and precious metals, viz. copper, lead, zinc, tin, bismuth, silver, nickel, gold, platinum, palladium and rhodium. Also a study was made of the relationship between metals in a car and their recycling.

Overview of Part II - Metal and Material Ecology

This part of the book discusses the sustainability of industrial ecology, the resource cycles of metals and role of technological knowledge are discussed. In this part, study background, relevance, the hypothesis, research questions and goals are introduced. The development of tools that assist in the dissemination of the knowledge to the stakeholders is discussed. Tools that facilitate communication between regulators, decision-makers and system designers through dissemination of technological knowledge, must be based upon an understandable logic originating from a solid technological base and must based upon interconnected material cycles as leading concept. Because neither in industrial ecology literature, nor in metallurgy literature, models have been reported that can connect the detailed models of engineers and holistic models of industrial ecology, it requires a new level of industrial ecology modelling.

- In **Chapter 2** the concept of sustainable development is explored. Industrial ecology is presented as a roadmap to approach sustainability. The concept and toolbox of industrial ecology are analyzed to examine its value for sustainability. In the toolbox, two types of approaches to support decision-making on industrial systems can be distinguished: descriptive approaches aimed at better understanding and quantification of the industrial systems, and prescriptive approaches that build on the descriptive approaches to evaluate industrial configurations and alternatives on their potential for sustainability.

- **Chapter 3** examines the value of descriptive industrial ecology approaches to contribute to improved understanding and quantification of the metal production and recycling systems. The resulting quantitative inventory and model approach will be used as a basis for the model of the metal resource cycles used in Chapter 5.
- In **Chapter 4** the metal cycles are investigated from prescriptive perspective, which addresses the analysis and control of materials and energy patterns through optimizing the ensemble of considerations that are involved. Bottlenecks are identified and the role of technological knowledge and models in the removal of these bottlenecks is examined.
- In **Chapter 5** an industrial ecology model of the interdependent industrial metal resource cycles is evaluated as a tool to assist decision-making on complex systems. The lead resource cycle is used as a case study. In the case-study, two complementary prescriptive strategies to reduce the environmental and human health impacts associated with the lead resource cycle are examined to illustrate what knowledge is necessary and whether industrial ecology approaches can provide this.
- Finally in **Chapter 6** the role of technology and technological knowledge is investigated by answering the different research questions through a synthesis of the different chapters.

1.4.2 Product Recycling as applied to the Car

The objective of the discussion of car recyling is to combine the resource cycle, the technology cycle and the life cycle of the car as represented by Figure 1.1 leading to the theory that describes the sustainable development of products. Recycling contributes to (a more) sustainable development of our society [50] by keeping raw materials within the resource cycle and saving energy (the production of metals from secondary resources has a much lower energy consumption compared to the production of primary resources). The recycling of materials minimises the amount of materials to be sent to land fill as final waste streams.

One of the objectives of this book is the development of a fundamental mathematical and technological basis for the description and understanding of recycling systems. These models provide a basis, which makes it possible to:

- *Optimise the recycling (rate) of passenger vehicles (and any other consumer product);*
- *Suggest a procedure for the calculation and prediction of the recycling rate of the present and future multi-material ultra-light car designs (and other consumer products), by which a modified ISO norm is being suggested;*
- *Provide a framework on which design software can be linked to recycling models in order to be able to apply design for recycling.*

This is only possible if the cycles in Figure 1.1 (Resource cycle, Technology cycle and Life cycle) are intersected and the models are fed by industrial data and knowledge. The objective of this work is to understand the complex interplay between systems dynamics, (sampling) statistics, separation efficiency (recovery), grade of recycling (intermediate) products, liberation, product design, system architecture, etc.

Fundamental mathematical and technological framework

Optimization of recycling; the prediction and calculation of recycling rates; and design for recycling can only be realised from a solid technological basis, in which fundamental knowledge of recycling systems is combined with that of the design of the product, as well as with the dynamic and statistically distributed parameters affecting recycling of cars. This is only possible with a detailed understanding of the total recycling system as a dynamic feedback system. This feedback system must embrace and link the economics, legislation, the physics and chemistry of the separation equipment, the product design and its liberation during shredding, statistics of mass flow and element data; and detailed reconciled mass balances, all as a function of time. In this work fundamental dynamic and recycling optimization models have been developed. These models combine theoretical knowledge of recycling processes and material characteristics of recycling (intermediate) products (material type, liberation, etc.) and their interconnected relation with the design of the product (material combinations and connections), within the framework of the dynamic and statistically distributed nature of the resource cycle. The developed mathematical models provide an essential tool for the calculation and prediction of the recycling rate of passenger vehicles in the design phase as well as for the optimization of their recycling.

Industrial data

It is essential for the practical use and reliability of the optimization and dynamic model that useful industrial data on the performance of processes and the flow and quality of materials should be available and have never really been measured properly. Industrial data is required to calibrate the recycling models that link these models to design software for the calculation and prediction of the recyclability of (future) multi-material ultra-light cars. Up to now, due to poor theoretical understanding of recycling systems, these data are not available. Furthermore, the lack of these data within a statistical framework makes any meaningful calculation of recycling rate impossible. The developed theory will be applied as a fundamental basis for proper collection of data, supported by a good mass balance based on data reconciliation, and the corresponding statistics. Only data reported within a statistical and theoretical framework can have a legal basis and can find their way into design software for cars. The statistics around the calculation of the recycling rate based on plant data indicates that the (calculations for the) recycling rates and requirements for type-approval of cars as imposed by legislation in Europe should also be based on a statistical basis and are meaningless if represented by a single value as is required at the moment.

Design for recycling

Design for recycling strategies, which are based on fundamental knowledge on the behaviour of materials and processes in the recycling system linked to design software, will result in design for liberation, design for physical separation and design for metal recovery, instead of applying often simple design for dismantling, or trivial or superficial design for recycling rules as is presently the situation!

System modelling

To realise the objectives of recycling a system engineering approach is required, which combines the description of the recycling system with the dynamic and distributed nature of the resource cycle system of passenger vehicles. This systems approach is essential for the optimization of the resource cycle, in order to avoid sub-optimization of subsets of parameters in this system. In this system approach, it is essential to link the disciplines depicted by the three cycles of Figure 1.1, of which the intersections capture the essence to realise the objectives of this book.

Contribution to the science of design for recycling

In this book fundamental theory has been developed to understand and optimise the complex interactions of the dynamics of the resource cycle with that of the processes and material flows and their characteristics in the recycling system of passenger vehicles, also in relation to the design of the car. This shows that recycling problems in relation to product design are complex and have to be solved from a fundamental system perspective and technological overview is required in addition to detailed know-how of the physical separation and metallurgical unit operations and material characteristics. Therefore the industrial practice, recycling theory and design in its system breadth and in its unit operation depth has to be understood to fully realise the objectives of legislation in view of a sustainable development of products. In this thesis seminal work for describing fundamentally and dynamically car recycling systems as well as the calculation of recycling rates on a fundamental and statistical manner has been developed. The theory of recycling has been developed based on the theory of classical minerals processing technology, systems engineering and process control theory, linked to the practice of recycling systems and available technology on physical separation and metallurgy. Therefore the dynamic and optimization models as developed in this thesis provide a tool for the development of the field of recycling complex consumer products into a more mature and fundamentally defined field than has been the case up till now. The models also provide a basis on which design software could be linked to recycling models. These models combine the theory and practice of recycling by linking the three interconnected cycles of Figure 1.1 and therefore provide a fundamental mathematical and technological framework:

- optimise the recycling (rate) of passenger vehicles, by addressing the complex relation between systems dynamics, (sampling) statistics, separation efficiency (recovery), grade of recycling (intermediate) products, liberation, product design, system architecture, etc.,
- calculate and predict the recycling rate,
- build and evaluate recycling scenarios of (future) car design and can e.g. be applied to find an optimum between dismantling and PST processing, taking cognisance of the required quality (grade) of the recycling (intermediate) products, being the input to e.g. metallurgical and thermal processing to optimise the recycling rate of the car,
- data collection on (recycling) plants to assess recycling systems, as well as to calibrated the developed models,
- indicates how design software could be linked to recycling models in future, and
- suggest a modified ISO norm.

The above will be based on fundamental technological knowledge and mathematical description of the behaviour of the processes, material and energy flows, particle size reduction, liberation and material quality in the recycling system in relation to the design of the car and the dynamic and statistical nature of the resource cycle.

Overview of Part III - Product Recycling as applied to the Car

This part of the book discusses various theoretical aspects of car recycling, using Car Recyling as an example to explain the various theoretical aspects involved in detail. this Chapter relies much on the understanding of Population Balance Modelling as briefly discussed in Appendix A.1.2.

- **Chapter 7** explains in detail the distributed nature of all properties (e.g. composition, size, liberation of materials, joints etc. i.e. population balance aspects) of the recycling system. This is quantified as distribution functions, which are then used to critisize the simplistic recycling legislation and the manner in which recycling rate calculations are made for this legislation. Various numerical examples are shown to illustrate the calculation of recycling rate calculation by the use of a Matlab.

- Continuing from Chapter 7, **Chapter 8** discusses how the distributed properties are embedded into a dynamic model to calculate the flow of materials through a recycling system in time, as a function of the distributed nature of all streams. An optimization model, that permits optimal recycling process choices to be made. is embedded into this dynamic model. Suitable models and software are provided to illustrate various calculations made for the recycling of cars.

- Crucial to recycling is the quantification of the liberation of materials during the shredding step of recycling. **Chapter 9** discusses in detail how liberation can be mathematically be defined so that it can be integrated into the various models discussed in Chapter 7 and Chapter 8, also linking to product design.

- **Chapter 10** discusses in detail an industrial experiment for the recycling of 1153 cars, in which many of the theoretical aspects discussed in **Part III** can be applied to calculate a statistically based recycling rate.

1.4.3 Aluminium Metallurgical and Recycling

This section provides a detailed overview of the recycling metallurgy of aluminium and a brief overview of primary aluminium production. Part IV also provides a detailed overview of different physical separation techniques that are used in the physical separation of scrap materials.

Overview of Part IV - Aluminium Metallurgy and Recycling

In **Part IV** the various theoretical and industrial issues around aluminium processing and recycling of Aluminium. This is a representative of the light metals to be used in cars in future, and is therefore discussed in detail.

- Both primary and second generation (secondary/scrap) raw materials for aluminium production are discussed in **Chapter 11**

- **Chapter 12** discusses the pre-treatment of aluminium containing material i.e. among others the physical separation of aluminium metal containing scrap/material (e.g. shredding, eddy current separation, sink-float to automatic sorting), compacting, heat treatment of scrap, etc.

- Continuing from Chapter 12, **Chapter 13** discusses the primary production of aluminium from ores (i.e. geological minerals and ores), followed by a discussion of aluminium metal production from metal containing recycled materials in (i.e. consumer minerals and scrap), touching on issues such as flux[1] viscosity and density, furnace types, sedimentation, melting yield of modern materials, emissions etc.
- **Chapter 14** discusses in detail how to simulate and industrial rotary furnace for the recycling of aluminium scrap. It is shown how to measure on the plant, how to reconcile the mass and energy balance, how losses and burn-off are calculated, and how subsequently all this information is integrated into a fluid flow model (CFD) of the furnace. This is done by integrating a population balance kinetic model for the scrap melting kinetics as a function of scrap type and particle size.

1.4.4 Various appendices of data and case studies

Various additional detailed information is summarised in **Appendix A** to **Appendix D**.

- **Appendix A.1** discusses the theory of particle systems including population balance modelling (PBM), sampling theory of Gy and separation theory e.g. the derivation of Grade-Recovery curves.
- **Appendix A.2** gives a brief overview over some aspects of metallurgical thermodynamics (three Laws) and also relevant references for more detailed information on this topic. Furthermore, examples illustrate the application of this to aspects of recycling metallurgy, which includes exergy calculations.
- **Appendix A.3** discusses in more detailed the modelling of transfer and fluid flow phenomena. Also various texts are referred to for more detailed information as well as examples by the authors that illustrate applications to recycling reactors.
- **Appendix B** provides a detailed inventory of industrial data for all the processes discusses in **Part II**, all obtained through data reconciliation. This is included to ensure that correct data are used for these processes in future to ensure that these maintain their important position in the **"Web of Metals"**.
- **Appendix C.1** and **Appendix C.2** provide source code for models in this book, while **Appendix C.3** provides to example spreadsheets for the optimization model. All these models are provided on the accompanying CD rom issued with this book. All relevant data and information used in the numerical examples are also present on the CD rom, providing a wealth of shareware data. (**Appendix D** contains the Simulink simulation model on the provided CD rom).

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[1] molten mixture of salt as opposed to a slag, which is a molten mixture of oxidic material

Part II

Metal and Material Ecology

Chapter 2

Sustainability and industrial ecology

In the last decades, sustainable development has become the cornerstone of environmental policy, and a leading principle for resource management. In this Chapter, the concept of sustainable development is explored (Sections 2.1 and 2.2). Industrial ecology is presented as a roadmap to approach sustainability (Section 2.3). The concept (Section 2.4) and toolbox of industrial ecology are analyzed (Section 2.5) to examine its value for sustainability (Section 2.6). The strength of industrial ecology is that it provides a context for analyzing the industrial economy at different levels of aggregation, from individual processes and products to the global material cycles. Its pitfall is that the different industrial ecology efforts must contribute to the overall environmental performance of the economy as a whole to enable a deliberate and rational progress towards sustainability. This is currently still not the case. The modelling of the physical economy and its interactions to the environment across the different levels is a first, but critical step in this direction. It is the objective of Part II to demonstrate how Figure 1.1 represents sustainability as a holistic integrated whole, illustrated in the context of complexly linked metals - the Web of Metals .

2.1 Sustainability or sustainable development?

Contrary to the belief of attributing ecological disaster exclusively to the industrial society, Mebratu [53] provides showed that ecological factors were key elements in the rise and fall of ancient civilizations and in major social transformations. The concern about sustainability has historical roots that can be traced back to at least the bible and the earliest writings of human societies, even though the word itself has come into fashion only in the past decades. Ehrenfeld [54] links sustainability to our instinctual survival patterns. He sees sustainability as or, better, unsustainability as a "social construct of collective fears and anxieties whose roots are the biological patterns that every one of us possesses". One of the first precursors to the concept of sustainable development dates back to the 1700s, when economist Thomas Robert Malthus observed limits to (population) growth caused by resource scarcity [53, 54, 55]. Together with David Ricardo he tried to fit his 'environmental limits thinking' into the (classic) economic tradition. In the 1800s, Stanley Jevons also observed limits to growth: the 'probable' exhaustion of coal mines due to ever-increasing energy consumption [55].

In the past three decades, the concern of 'running out' was complemented with the concern

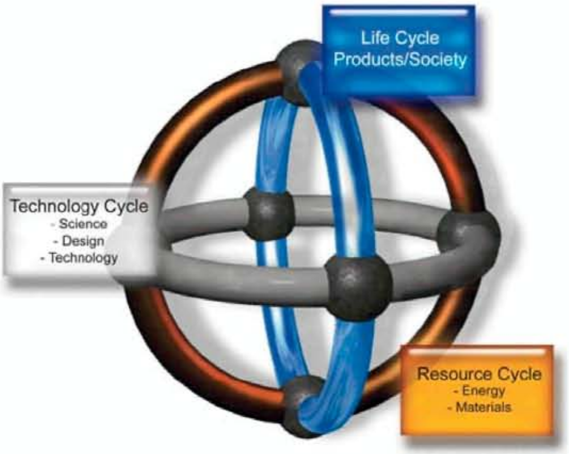

Figure 2.1: Sustainability demonstrated by linking among others the three depicted cycles in the context of metals - conntected through the mine, the product and subsequently recycled back into the material cycle [51, 52]

that the ever-increasing quantities of waste produced are overstressing the capacity of ecosystems. Meadows et al. [56] in their book *Limits to growth* questioned the 'sustainability' of the whole of industrial civilization given the finiteness of the planet's capacity to provide material inputs to modern economies and to assimilate their waste outputs and emissions. These two concerns are at the basis of the concept of sustainability, which has become a key objective in most international and national policies and many corporate strategies. More recently, the discussion on sustainability and limits to growth also included social and political issues, because of the widespread belief that environmental problems can not effectively be solved if the political and social problems are ignored (and vice versa).

The inclusion of political and social issues in the definition of sustainability significantly adds to the difficulty of using the concept, let alone of defining it precisely. Sustainability involves determining many balances: between societal needs and economic development on the one hand, and the environmental capacity and value on the other, between the needs of different countries, or between short-term and long-term interests. The United Nations concept of 'sustainable development' is a widely accepted interpretation of sustainability that addresses the complex of environmental, technical, economical, political and social problems. It is based on what Brown [57] in 1981 defined a sustainable society: "one that satisfies its needs without diminishing the prospects of future generations". The United Nations Commission on Environment and Development through the Brundtland Report popularized the concept of sustainability in 1987. The report, entitled *Our Common Future*, provided the definition of sustainability, viz. Sustainable development: development that "meets the needs of the present without compromising the ability of future generations to meet theirs" [50]. Five years later, this concept was formalized at the United Nations Conference on Environment and Development [58]. The concept of sustainable development is anthropocentric, which means focused on the human species and considering all other life as it contributes to this end [14]. The concept of sustainable development contains within it two key concepts:

- "the concepts of needs, in particular the essential needs of the world's poor, to which overriding priority should be given"

- "the idea of limitations imposed by the state of technology and social organization on the environment's ability to meet present and future needs" [50].

Simply put, the first concept means global solidarity in meeting the present and future needs. The developed nations should reduce their disproportionate share in the use of the earth's capabilities, to enable the other, developing nations to meet their own needs while maintaining the quality of their environment. The rationale for this 'intragenerational' equity is that if developing nations would develop to the same resource intensity as the current developed countries, meeting the needs of future generation would pose far greater limitations on the state of technology and social organization, if possible at all. However, the realization of a fairer distribution of resources and wealth is complicated. The wealthy, developed countries that use resources will be difficult to convince giving up part of their wealth. Although it is widely accepted, sustainable development is just an interpretation of sustainability . Allenby [14] for example argues that equity has yet to be achieved through human history, which suggests that it may be unlikely in the near future. He views sustainable development as just one of the combinations of technology, social organization, and environment that potentially yield a sustainable global society, and it may well not be the most likely. The broad acceptance of sustainable development has unfortunately retarded the debate about other possible sustainable futures and the need for choice among the 'universe' of other sustainable futures. Nevertheless, it can be an important guide to significant conceptual progress. Other authors question the feasibility of sustainable development as a guide to significant conceptual progress. They perceive the concept as vague and elusive. Instead of guiding conceptual progress, the concept runs the risk of being devaluated to a cliché. Daly [59] and Mebratu [53] observe that the vagueness of the concept of sustainable development allowed for its broad acceptance and consensus on its desirability. However, it also led to a large 'political battle' for influence over our future by linking interpretations to the concept. In trying to win the battle, the emphasis of conceptual development of the concept has shifted from logical coherence to that of semantics. For developing our understanding of the concept and using it as an important guide to achieving a sustainable world, strengthening the logical coherency of the concept (by overcoming the influence of the different battling groups) is essential. Despite of the range of positions in the debate on sustainability, it is clear that one should be careful to equate sustainable development with sustainability . In Part II, sustainability is defined according to Ehrenfeld [54]. He tries to define sustainability without limiting himself to a subset of the 'universe' of other sustainable futures. "Sustainability is a possibility that humans and other life will flourish on the earth forever." This definition is a powerful way of thinking about sustainability, and overcoming differences in interpretation. It is clearly insufficient as a guide to significant conceptual progress, however. Ehrenfeld therefore suggest a more practical working definition of sustainability. "Sustainability is a possible way of living or being in which individuals, firms, governments, and other institutions act responsibly in taking care of the future as it belonged to them today, equitably sharing the ecological resources on which the survival of humans and other species depends, and assuring that all who live today and in the future are able to flourish - that is, satisfy their needs and aspirations."

2.2 Achieving Sustainability

Although the basic ideas of sustainability are old and simple, sustainability proved a remarkably difficult concept to use and define precisely. Despite evident value of sustainability, it is often impossible to deduce concrete decisions for specific cases from the concept of sustainability. However, this does not mean that the concept is of no value, but it rather indicates the complexity of the concept. There are two fundamental reasons for the difficulty using sustainability: nobody knows what a sustainable society would be like, and or how to achieve it. Thus to achieve sustainability, one first must examine where to go to, and secondly how to get there.

2.2.1 Going where?

What would a sustainable global economy look like? The finite resilience of ecosystems, for example, is a key concern in all definitions of sustainability. All life depends on the environment, and the functions and viability of natural systems. Therefore, the industrial civilizations and the environment are interrelated and must become compatible to survive. Compatible implies a use of resources, and a generation of wastes and emissions at a level that is not likely to cause serious damage to the environment. Using and precisely defining, however, is complex: what extent of damage is acceptable? Scientific knowledge and understanding alone are often insufficient for determining unambiguously a maximum compatible use of resources, or a total pollution limit. First, the effects of human interventions on the environment are still not well understood, and the effects of interventions may only become visible with significant delays, and may be irreversible. Furthermore, nature possesses self-regulating mechanisms, which are composed of a complex web of positive and negative feedback systems . Consequently, nature itself can also develop as a reaction to changing conditions. In polluted areas, different types of ecosystems may develop than in not polluted areas, with different characteristics, assimilation capacities or pollution thresholds. Due to these dynamics, and the complexity of natural processes, the assimilation capacity and resilience of environmental processes are very difficult to determine, and therefore to set a maximum permissible use of resources or a total pollution limit. Moreover, is there a difference between one damage or another? Is ozone layer destruction worse than the greenhouse effect or local pollution of the groundwater? Also, must we consider 'damage' as a reduction of the opportunities or available resources for human activities, or has nature itself an intrinsic value as well, which should be protected? Conservation of the intrinsic value of nature will often be compatible with safeguarding the environment for human interests, but not necessarily always. The interpretation (operationalisation) of damage from a human perspective is prominent in most perspectives of sustainability. The damage to the environment is thus acceptable if future generations can still meet their needs and flourish. This poses limitations not only on the state of technology, but also on the social organization and on the environment. Perhaps more important are the different mental models concerning the resilience of natural systems (to human interventions), and consequently what action should be taken in what time frame. Allenby [14] distinguishes four mental models and types of action. On the two extremes are the ones that belief that nature is virtually immune to human perturbation (action: continuation of status quo) and the ones that belief that nature is extremely fragile (radical ecology, action: immediate return to low technology). The centrists positions are taken by the ones that view nature as robust, but within distinct limits, that when transgressed can result in a sudden shift to another meta-stable situation. Dependent on how stable the meta-stable situation is assumed to be, the positions range from the use of appropriate technology, which is low-tech where possible (deep ecology), to reliance on technological evolution within environmental constraints and no preference for low-tech unless environmentally desirable (industrial ecology) . In sustainable development, nature is also considered robust. It aims to counter the absolute impacts generated by economic growth by increased eco-efficiency: more product or service for the same or less negative environmental impact. Finally, sustainability is so easy to understand, but so difficult to define, because it reaches the core of human nature. Determining a maximum damage limit is one thing, determining the conditions under which humans (and other life) will flourish on the earth is another. It involves reflection on our needs. Ehrenfeld's notion of flourishing is closely linked on Fromm's concepts of having and being. In *To Have or To Be*, Fromm [60] distinguishes two fundamental modes of human existence. The 'having' paradigm, which has become the dominant mode in modern industrial cultures, has turned pathological, and only a shift to the radical, alternate 'being' mode can save both the human kind and the natural world[1]. Not only it is doubtful whether increased eco-efficiency can counter the impact of continued economic and material growth emerging from the having mode, quality of life cannot be achieved with 'having' alone [61, 62, 63]. Sustainability thus requires a change of heart. Only if humans can learn to value 'being' over 'having', sustainability can follow [54].

2.2.2 Getting there

Even if scientific knowledge on what damage is acceptable is, or becomes available, even if we can define our needs based on the having paradigm, the next problem is how to use this information to develop a sustainable global economy. It is likely that realization of sustainability will require some (global) consensus on the balance between the optimal use of the environment from a social and economic point of view with maintaining the intrinsic value of nature, if on some point there is a conflict between the two. Or that it will require consensus on the distribution of the use of environmental resources and the burden of reducing pollution over different industrial systems, or between countries, and how to reach that distribution. Consensus on the latter in particular is critical to develop a sustainable global economy. It is well accepted that sustainable development can be achieved easier when population is stabilized at a level consistent with the productive (but also assimilation) capacity of the ecosystem earth. If a consistent population level can scientifically be determined, this leaves the tough question of how to 'allocate' the population stabilization or reduction between countries. Particular, considering the rational behaviour at an individual level gives rise to irrational level on the overall level (prisoner dilemma). The earth is increasingly an engineered world in which human choice and technology determine the structure not only of human lives and environments, but for all life on the planet. Sustainable development or sustainability is an emerging property in systems terms , which means among others: that sustainability is a property of the system as a whole and that one can not know that the system is sustainable until in fact sustainability has been achieved. The concept of a sustainable subsystem in an unsustainable global system is fundamentally an oxymoron, i.e. it combines two opposite ideas and is thus impossible. The sustainability of any subsystem such as a community within the global system can only be defined in terms of the global system. The degree and kind of controls and knowledge that controlling such a complex interlinked and highly non-linear system would imply, however, are currently beyond the state-of-art [14]. Because of the systemic character of sustainability, the western concepts of reductionist science and linear short term and obvious causality

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[1] The 'having' mode concentrates on material possession, acquisitiveness, power, and aggression and is the basis of such universal evils as greed, envy, and violence. The 'being' mode is based on love, in the pleasure of sharing, and in meaningful and productive rather than wasteful activity.

will have to be augmented by more systems-based, comprehensive approaches to develop the appropriate tools. Perhaps to the most important notion for achieving sustainability is that there is no getting 'there' . Sustainability is a continuous process, not an endpoint or a specific state of a system. As human culture, technologies, population levels and natural systems evolve, so will the parameters of sustainability. Similar to nature, society possesses all kinds of self-regulating mechanisms, which are composed of a complex web of positive and negative feedback systems. Change induces change. Virtually every modern institution - the national state, major religions, the private firms, academic institutions, the family etc. - change at an unparalleled, but little recognized rate. Because of these developments, the limitations to social organization must change as well. Evolution towards an economically and environmentally efficient economy will differentially favour certain industrial sectors and technological systems, and disfavour others. Thus, sustainability has a temporal component: sustainable for how long and within what time frame? It is about a co-evolution of human and natural activities. A continuously developing world that slips in and out desirable states that are each sustainable over some time frame, a sort of 'punctuated equilibrium' [64, 65, 14, 66, 67]. Only by understanding sustainability as a continuous process, society can direct their research and resources in the appropriate direction. Despite the complexity of defining, using and realizing sustainability, it is assumed in this Part II that under optimal conditions some kind of reasonable and acceptable path towards a desirable, environmentally and economically efficient sustainable global economy does exist [14]. The next section discusses industrial ecology as a possible roadmap to restructure industrial activities along this reasonable and acceptable path.

2.3 Industrial Ecology

In the first textbook on industrial ecology Graedel and Allenby [12] define the essence of industrial ecology as follows:

> *"Industrial ecology is the means by which humanity can deliberately and rationally approach a desirable carrying capacity, given continued economic, cultural, and technological evolution. The concept requires that an industrial system be viewed not in isolation from its surroundings, but in concert with them. It is a systems view in which one seeks to optimize the total material cycle from virgin material, to finished material, to components, to product, to obsolete product, and to ultimate disposal. Factors to be optimized include resources, energy, and capital."*

The words deliberately and rationally in the above definition indicate that the intent of the field of industrial ecology is to provide the technological and scientific basis for a considered path towards global sustainability , in contrast to unplanned, precipitous and potentially quite costly and disastrous alternatives [12]. Industrial ecology is therefore sometimes regarded as the science of sustainability. Although industrial ecology is a relatively young field, the concept of industrial ecology is not new. There is little doubt that the ideas of industrial ecology existed well before the expression, which began to appear in the literature of the 1970s [68]. Erkman et al. [68] found that the concept of industrial ecosystems was already clearly present in the writings of system ecologist such as Odum and Hall [69, 70]. O'Rourke et al. [71] trace the ideas back to the early seventies, for example to Barry Commoner's seminar book *The closing circle* [72], which asserted that "present productive technologies need to be redesigned to conform as closely as possible to ecological requirements". However, in the course of the past thirty years the several attempts to launch this new field yielded only marginal success [68]. That is until 1989 when Frosch and Gallopoulos published an article entitled *Strategies for Manufacturing* in Scientific American [73]. The article sparked the current development of industrial ecology, and inspired many authors to write articles spreading their ideas in various academic and business circles. Among them, it was notably Tibbs [74] who translated the ideas in the article into the language and rhetoric of the business world, which spread Frosch and Gallopoulos' ideas throughout the business world. The ideas on 'industrial metabolism' of Robert Ayres provided means to support the decision-making on industrial ecological principles to key decision-makers, such as regulators, industrial managers or engineers [75, 76]. Ayres suggested to describe the metabolism of the industrial system through detailed 'material balances', which could be compiled at different spatial scales, e.g. for a production unit, such as a factory, or a geographic unit as small as a village or as large as a continent. The first university handbook of Industrial Ecology in 1995 [12] marked the broad acceptance of industrial ecology. The launch of the Journal of Industrial Ecology in 1997 can be seen as official recognition of the academic community of this new field.

2.4 The concept

Industrial ecology is a new concept emerging in the evolution of environmental management paradigms [77]. Because of its early stage of development, it is still mostly a cluster of concepts, tools, metaphors and exemplary applications and objectives, and has no clear demarcation of the field [78]. This review should therefore be seen as a somewhat 'impressionistic' painting of industrial ecology and its applications, rather than a comprehensive picture of the field. The expression Industrial Ecology (IE), a combination of 'industry' and 'ecology', expresses some of the content of the field [78]. These two notions are the base colours in the painting of this new concept.

2.4.1 The industrial notion

The first word 'industrial' in industrial ecology states the focus on industrial processes. Many in the field of industrial ecology see industrial (or technological) change as the only means that offers a possibility of reducing the fundamental environmental impacts of human economic activity, at least in the short term. The importance of industrial change can be explained with the so-called master equation of sustainability. The master equation focuses thinking on the most efficient response that society can make to environmental stresses by examining the predominant factors involved in generating those stresses [79, 72, 40, 12, 14, 80]. It is not difficult to imagine that the stresses on many aspects of the earth system are predominantly influenced by the size of the population, and by the standard of living that that population desires. The master Eq. 2.1 is a well-known expression of those driving forces.

$$I = P \cdot A \cdot T \tag{2.1}$$

In which

I = Impact
P = Population
A = Affluence (or Wealth indicated by consumption per capita)
T = Technology (indicated by the level of Impact per consumption)

To understand the role of industries, the three right-hand terms, and their probable change with time must be understood. The first two terms in the equation, viz. P and A are strongly tending upwards [14, 40, 12, 81]. Of these three categories of driving forces, population produces the most controversy. It is, however, one of the few variables for which worldwide data of reasonable accuracy are available, providing a basis for statistical assessments of its role in various kinds of environmental change. Despite diseases as aids or other epidemics, the global population is expected to grow substantially, mostly in the developing countries. Since 1970, population has already grown eight-fold. Projections of a peak in population of eight to twelve billion persons, or even more in this century are not regarded as unrealistic by demographers [81, 14]. At the present time, the 'quality of life', which is what A in Equation 2.1 really refers to, is almost universally defined in terms of ability to appropriate goods and materials. 'Having' things, in particular status symbols such as automobiles, is an important goal for most of humanity [54, 40]. It is unlikely that the world would be able to support a world economy if today's Western production and consumption levels are adopted by the developing countries, in particular given the expected growth in population. This may not be for reasons of absolute scarcity, new sources for materials and substitutes will be found as prices shift. The cumulative environmental impact of material cycling through the world economy can also destabilize, or (unacceptably) perturb existing natural systems [14]. Because of the strongly trend upwards of population and wealth factors in the equation, industrial ecology focuses on the third right hand term T: Technology. This is the only remaining factor that, at least in the short term, can offer a possibility of reducing the fundamental environmental impacts of human economic activity[2]. It represents the degree to which technology is available to meet human needs without serious environmental consequences. Chertow [80] tracked the various forms the IPAT equation has taken over 30 years as a means of examining an underlying shift among many environmentalists toward a more accepting view of the role technology can play in sustainable development. She concludes that although the IPAT equation was once used to determine which single variable was the most damaging to the environment, an industrial ecology view reverses this usage, recognizing that increases in population and affluence can, in many cases, be balanced by improvements to the environment offered by technological systems. Many in the field of industrial ecology view on the one hand industry as an important source of environmental damage, but on the other hand technological or industrial development as a central means of solving environmental problems. Industries represent an important source of technological expertise critical to execution of environmentally informed design of products and processes. Furthermore, business is considered both a policy-maker and policy-taker [78]. Although this view is widely shared within the field, the degree to which technological innovation will sufficiently solve the problems, and for how long, is still a subject of ongoing debate [78]. The master equation also shows a limitation of the industrial focus of industrial ecology. Technological evolution can buy time for cultural/social evolution, but it is not a substitute. A typical example illustrating this is the development of cars. The improvement in car technology has not dramatically reduced emission and fuel consumption because people drive their cars further, and choose less efficient models [40]. Thus technology here is both part of the solution and part of the problem, which illustrates the need for critical attitude towards technology as argued in the previous chapter.

2.4.2 The ecological notion

The ecological notion applies to the field in at least two ways:

1. Natural ecosystems are used as a model for industrial activity

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[2] Chertow [80] concludes this industrial ecologist's vision on technology is partly pragmatic (technological variables often seem easier to manage than human behaviour) and partly a technocratic (belief in scientific advance)

2. human technological activity is placed in the context of the ecosystems that support it.

The different definitions of industrial ecology differ in the way that emphasize one of these ways. Graedel [82] emphasizes the latter notion by defining industrial ecology as a multidisciplinary, "system-oriented concept [which] suggests that industrial design and manufacturing processes are not performed in isolation from their surroundings". Contextual analysis of technological activities has a strong link to forward-looking research and practice in the field of industrial ecology, acknowledging that it is important to avoid environmental problems that are irreversible, or too costly to remedy. Frosch and Gallopoulos [73] focus on the first notion and describe industrial ecology as a concept in engineering and management whereby it is attempted to operate industrial estates as ecosystems through adaptation of typical ecosystem features: feedback (control) loops , minimal use of resources and minimal production of wastes by cascading the use of resources and energy. Arguably, the notion ecological also applies to the field in a third way. Industrial ecology also uses concepts, approaches and methodology from biological ecology. Analogous to ecology, industrial ecology emphasizes the need for systems perspectives. This perspective is manifested in different forms: the use of life cycle perspectives, of material flow and energy flow analysis, of systems modelling. Industrial ecology has a comparable sympathy for multidisciplinary and interdisciplinary research and analyses [78]. Den Hond [83] considered the biological analogy the most important, conceptual contribution of industrial ecology. Industrial ecology assumes that the functioning of ecosystems provides examples, ideas and prescriptions of how to design and operate sustainable industrial systems [84]. The biological analogy involves a comparison of living ecosystems found in nature to industrial activities. Interestingly, the analogy is used the other way around. Microbiologists draw the analogy with industrial manufacturing processes when modelling metabolic pathways within the cell [85]. In the frame below, ecosystem and ecology are discussed as a basis to explore the biological analogy.

Cadre 2.1
Ecosystems

An ecosystem is a functional unit in nature composed of:

- *abiotic constituents, all non-living elements such as minerals, climate, soil, water, sunlight,*
- *biotic constituents, all its living elements such as mammals, plants, insects, fungi, and*
- *their interactions that link the abiotic and biotic constituents, viz. the cascaded energy flows through the ecosystem, and the cycling of nutrients within the ecosystem.*

Each organism in an ecosystem or the waste it produces is food for others. Specialized species convert wastes into the minerals required by the 'primary producers'. Mature ecosystems contain high biodiversity of species, organized in complex webs of relationships. In these ecosystem networks, each individual in a species acts independently, yet its activity patterns cooperatively mesh with the patterns of other species. The result is a complex dynamic network where every material is used in the anabolism and catabolism of life, and the material cycles are largely closed. Ecology, the study of living ecosystems, therefore stresses that all the elements of an ecosystem form part of an integral, dynamic network in which each element interacts directly or indirectly with all others, and thereby affect the function of the system as a whole. The many relationships are maintained through self-organizing process *that keep efficiency and productivity of ecosystems in dynamic balance with their resilience to environmental perturbations ('autpoeisis' and 'homeostasis' [86, 72, 13, 10]). A change in the number and populations of species affects the operation of the ecosystem as a whole, and allows it to adapt to changing conditions. Ecosystems are thus flexible, ever-fluctuating networks according to Capra [10]. The more 'network variables' (e.g. number of species, size of populations) are kept fluctuating; the greater its flexibility; i.e. the greater its ability to adapt to changing conditions. A diverse ecosystem will be flexible, because it contains more network variables that can fluctuate: many species have overlapping ecological functions that can partially replace and complement one other. This actual adaptability or resilience is a consequence of its multiple feedback loops. These tend to bring the ecosystem back into balance, whenever there is a deviation from the norm, due to changing environmental conditions. Darwin's natural selection is an example of such a feedback mechanism. The best-adapted or fittest species flourish most and their number accumulates (positive feedback). The less adapted species must compete over the remaining resources, and their number will decrease. Eventually, this may lead to extinction, unless the species evolve or find ecological niches (negative feedback). However, as environmental conditions change over time, the relative fitness of organisms also changes. As a result, the species and populations of the different species adapt (old species become extinct or new species evolve) to maximize the efficiency and productivity of the ecosystem under the new conditions. As such, the environmental conditions limit the extent to which the different plant and animal populations can grow. A balance in positive and negative feedback loops are of great importance for stability in all biological systems. Most growth phenomena in a biological setting involve positive feedback loops. Such a process of growth tends to increase very rapidly (viz. exponential growth) until it reaches a population in which other factors become important. These will typically act to limit the growth in a way, which can often be recognized as a negative feedback loop. In ecosystems with unbalanced positive and negative feedback - e.g. excessive amounts of a single or a few nutrients, or the absence of predators - can lead to exponential growth of a single or a few species, which can lead to the extinction of other species, and eventually even to ecosystem collapse and succession. In particular, excessive amounts of plant nutrients (primarily phosphorus, nitrogen, and carbon) can lead to 'eutrophication' or 'nutrient pollution*[3]*. Finally, it is important to note that the dimensions of ecosystems vary from very small, the oral cavity of man or a segment of man's intestine, to very large, tropical rainforest or lake [87]. The largest ecosystem is the 'natural' earth itself, which in turn can be considered to behave like an organism [88, 89]).*

Graedel and Allenby [12] offered a typology of ecosystems that can be used as models for industrial activity in industrial ecology. They distinguished three types, dependent on the degree to which they rely on external inputs (energy and resources): Type I is the most linear system, and the most reliant on external input. These systems can exist in presence of unlimited resources, and unlimited sinks for wastes, for example when the number of organisms is small and the use of resources has no or negligible impacts on the availability of resources. (Examples: modern agricultural practices, which are based on large mono-cultures or biotechnological processes.) However, when the numbers of organisms increase, the external inputs and sinks will be influenced, which constrains the availability of sources and sinks. Type II system includes feedback loops and cycling that enable a more efficient use of

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[3] A well-known source was the phosphorus in sewage when detergents still contained large amounts of phosphates. The phosphates acted as water softeners to improve the cleaning action, but also as powerful stimulants to algal growth. The resulting excessive growth of algae among others blocked sunlight and led to oxygen depletion. As a result, it led to changes in ecosystem structure: bottom fauna and fish species disappeared (and/or were replaced by species more resistant to the new conditions).

available external inputs and sinks. These (quasi-cyclic) systems are more efficient than the linear, but eventually run out of inputs and sinks, and thus are not sustainable on the long run. (Example: developing ecosystems, fish tank or to a lesser extent green houses). Type III are completely cyclic systems were external resources are completely recycled (closed material cycles). These systems need only an external energy source to drive the resource cycles, and can be sustainable if a sustainable source of energy is available. Energy cascaded to maximize utilization of energy available for growth and maintenance of the system. Most (mature) 'natural' ecosystems approach type III, and idealistically the largest ecosystem earth can be considered as a type III system. Their efficient cycling of resources is considered ideal for industrial systems at many scales, and explains the strong emphasis of industrial ecology on closing the material cycles. "Industrial ecology, in its implementation, is intended to accomplish the evolution from Type I to Type II and ultimately to Type III by understanding the interplay of processes and flows, and by optimizing the ensemble of considerations that are involved" [12]. This explains the interest in the field of industrial ecology for strategies aiming at closed loop systems, detoxification and dematerialization[4], but also multidisciplinary and interdisciplinary research and analyses. Graedel and Allenby observe that the 'nodes' in industrial ecosystems (viz. the material extractor or grower, the materials processor or manufacturer, the user, and the scavenger or waste processor) have to be attuned to one another to accomplish the desired evolution. The analogy provides also other suggestions for organizing industrial activity. Biodiversity and interconnectedness in ecosystems points at the fact that only networks can be sustainable; a single organism, company, or firm can never be sustainable [84]. According to Ehrenfeld [84] besides closed looped material cycles and cascading energy utilization, the ecosystem characteristics that have to be achieved are approximation of a "thermodynamic" steady state of minimum entropy generation and dynamical stability. Ecosystems must therefore continuously adapt to changes in their surroundings, or else they vanish by ecosystem transformation, or ecological succession. Ecosystems adapt by natural selection; the process by which species of animals and plants that are best adapted to their environment survive and reproduce, while those that are less adapted die out. Ecosystems survive by the continuous adaptation of all the organisms in ecosystems. Bertalanffy [26, 27] speaks of 'Fliessgleichgewicht' (literally flowing balance) to describe this dynamic stability, the coexistence of balance and flow, of structure and change, in all forms of life [90, 91]. By analogy, industrial ecosystems should be dynamically stable as well; they must meet continuously the needs of society, but be able to react dynamically on changes in its environment, by rerouting relationships between its components, or by changing the configuration of its components. An important lesson for controlling such systems is that the many relationships are maintained through self-organizing process, not top-down control [13]. Côté [92] recently suggested that more industrial 'biodiversity' (scavengers and decomposers) "could increase the cycling of other materials that may be available and valuable in smaller quantities", and should also increase the resilience of eco-industrial parks such as Kalundborg. The biological analogy is also explored in other directions, for example, its application to products as a source for design inspiration, a framework for characterization of product relationships, and a model for organizational interactions in technological webs [78].

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[4] The evolution to a Type II or III system not only involves closing the material cycles, but also to use fewer resources to accomplish tasks. Dematerialization refers to reduction of the amount of material use to accomplish a task (sector, national, regional or global level), and eco-efficiency refers to reduced use of environmental resources given a certain level of output (firm level). Detoxification refers to the use of less damaging products, substances and materials to decrease the impact of products, substances and materials that cannot be properly recycled.

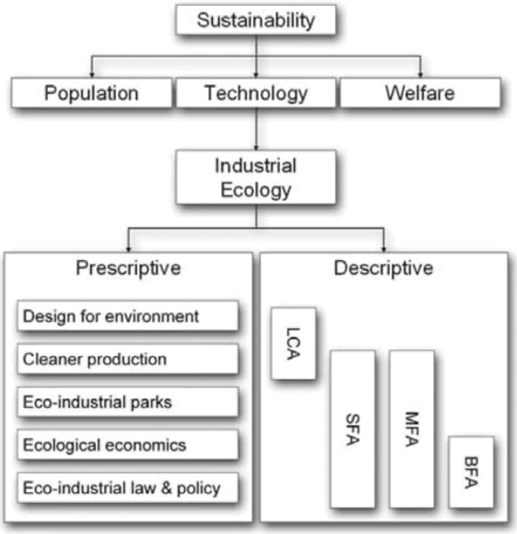

Figure 2.2: Industrial ecology approaches and examples of their applications (tools)

2.5 The toolbox

Given the wide scope of the field, it is not surprising that different approaches present themselves. In this section, it is attempted to provide an overview of the toolbox of industrial ecology[5]. The description of industrial ecology at the back of the journal reveals two groups of approaches, viz. descriptive "Industrial ecology systematically examines local, regional, and global uses and flows of materials and energy in products, processes, industrial sectors and economies" and prescriptive "It focuses on the potential role of industry in reducing environmental burdens throughout the entire product life cycle". A distinction can be thus made between (i) prescriptive approaches, eco-design studies that address the control of the patterns of flows and processes through optimizing the ensemble of considerations that are involved, and (ii) descriptive approaches, systemic analysis studies that describe and analyse the interplay of processes and flows (see e.g. Lifset and Graedel [78], Den Hond [83], O'Rourke et al. [71])[6]. Figure 2.2 shows examples of the applications (tools) of both approaches. These are discussed the sections below.

2.5.1 Prescriptive approaches

The prescriptive approaches involve the analysis of the influence of technical, economic, political, regulatory, and social factors on the flow, use, and the transformation of resources,

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[5] Note that the review is not a complete overview of all available tools, but rather gives an overview of the range of tools available. It is based on a literature search of the journal of Industrial Ecology, the critical reviews of Den Hond [83] and O'Rourke et al. [71], the special issue of the journal of cleaner Production, and handbooks of Industrial Ecology [15, 13, 14, 11, 12, 40].

[6] In addition to this application-oriented conceptualization of industrial ecology, other conceptualisations are possible also, e.g. based on the variety of system levels at which industrial ecology operates: (i) firm level, (ii) between firms, (iii) regional and global (see e.g Lifset and Graedel [78]).

notably how these factors can be put to use to steer the development and patterns of material and energy flows. Generic and specific activities can be distinguished.

Strengths

The prescriptive approaches in industrial ecology may be seen as responses to a nested set of challenges from the individual products development to global policies and legislation. Prescriptive approaches assist design and management across these levels to 'deliberately and rationally' approach sustainability. Examples of these prescriptive approaches across the different levels of design include: design for environment at product level, pollution prevention at process level, development of eco-industrial parks at regional level, and finally the development of economics theory, regulation, and market conditions at national or global level. Design for Environment (DfE) designates a practice by which environmental considerations are integrated into process and product design, and materials and technology choices [93]. DfE has a close link with Life Cycle Assessment (see Section 2.5.2). Pollution prevention (or synonymously Cleaner production) is a well-developed field of environmental engineering that focuses particularly on the design of industrial processes. Pollution prevention does not generally address the relationships between industrial plants, but its design for environment tools could be very helpful in providing a systemic perspective for weighing trade-offs between competing options for change [13]. Industrial ecology can also be applied to organizations, e.g. of industrial process communities (industrial ecosystems), and to the rules and incentives of the organization process (development of the regulatory landscape, and market conditions). An eco-industrial park is a community of industrial plants that is based on the integrated model of an ecosystem. In the traditional model of industrial activity, manufacturing processes take in raw materials and generate products to be sold plus waste to be disposed of. In the ecosystem model, consumption of energy and materials is optimized, generation of waste is minimized and residues of one process serve as input for others [73]. An often-cited example is the spontaneous, but slow development of industrial symbiosis at Kalundborg. The development of policy and legislation is an essential condition for successful implementation of industrial ecology at lower system scales (products, processes, eco-industrial parks). Private entities, acting alone, can make some progress, but can not compensate for wider systems-based barriers to progress towards sustainability. Therefore, boundary conditions need to be designed to encourage appropriate behaviour on the part of the producers and consumers, and the conditions must be laid down in legislation and policy. In the first handbook of industrial ecology, Graedel and Allenby [12] already recognized and discussed the role of governments, policy and legislation for the implementation of industrial ecology. Examples of more extensive, recent analyses in this area include Lowe et al. [13] and Allenby [14]. The prescriptive approaches have tended to focus on design for environment, (technology) policy and legislation. Industrial ecologist discuss broader strategy occasionally in informal settings. In general the literature does not reflect this discussion except in side comments (see e.g. Lowe et al. [13], Graedel and Allenby [12]). Economic theory is critical to the implementation of industrial ecology. Many studies in the industrial ecology (IE) literature share the premise that material and energy flows can be deliberately and rationally influenced by (i) setting the 'right' prices (internalizing environmental and social externalities), (ii) providing the 'right' information (showing the environmental consequences of their actions) and (iii) setting the incentives and boundary conditions for activities in regulation [83, 71]. In this way, the 'invisible hand of the market' can co-ordinate decisions at different scales (individual, firm, regional, national or global) and thus provide the context for the co-ordination of the different tools. This belief in self-organizing capacity of (competitive) markets may be linked to the self-organization (or 'autopoeisis') of natural ecosystems through decentralized processes and survival of the most adapted. To achieve a sustainable global society, there is a need for extending and integrating the study and management of "nature's household" (ecology) and "humankind's household" (economics)[7]. The journal of Ecological Economics started in 1989 as recognition that this integration is necessary "because conceptual and professional isolation have led to economic and environmental policies which are mutually destructive rather than reinforcing in the long term" (Journal of Ecological Economics). The journal aims to provide a forum for new issues in this area, which are rapidly emerging from exploring the interactions between economics and (industrial) ecology.

Weaknesses

To deliberately and rationally advance to sustainability, the combined prescriptive approaches must contribute to the overall environmental performance of the system as a whole. This involves co-ordinated improvement of products, processes and process combinations, and the development of regulation and market conditions. This is currently not the case. Rather, the objectives and outcomes of the different prescriptive tools can be conflicting, and, as a consequence, do not contribute to an improved overall performance. For example, the conversion of waste into by-products can conflict with the emphasis on waste reduction in pollution prevention, and vice versa pollution prevention based regulations can inhibit the reuse of waste, even within a company (see e.g. Lowe et al. [13]). An essential question for industrial ecology is, therefore, how to co-ordinate the tools that operate at different levels, and consider different aspects of the overall IE strategies. In economic systems, price mechanisms guide material and energy use and allocation of outputs, and co-ordinate the actions of the actors. In this way, the 'invisible hand of the market' can co-ordinate decisions at different scales (individual, firm, regional, national or global) and thus provides the context for the co-ordination of the different tools. However, consumers and firms are only partly informed by price, information and regulation. External conditions and internal motivations, such as strategic decision-making to eliminate direct opponents (see Kuit et al. [95]) also play important roles. The market is an existing, but flawed tool for co-ordinating decentralized decision-making across different system levels. In order to effectively co-ordinate the prescriptive activities coordinating, industrial ecology calls for a preferably objective framework. Market designs must also reflect the physical reality of the underlying system in order to co-ordinate decisions effectively [96]. The current design of the European electricity markets does not sufficiently do so and as a result can not ensure the market goal, the reliability of the electricity supply. This suggests that quantitative descriptions of the underlying physical systems could provide for such framework. The eco-industrial park Kalundborg is perhaps the best-known application

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[7] Among others Costanza et al. [94] realized that the value of ecosystems are not 'fully' captured in commercial markets or adequately quantified in terms comparable with economic services and manufactured capital. Consequently, they are often given too little weight in policy decisions, which may be the ultimate cause of the development into the present consumption society. Capturing the value of ecosystems is hindered by practical problems. Because data on impacts are scarce and uncertain, it is difficult quantifying social and environmental costs in terms of costs and benefits [12]. In addition, the economic translation of price signals into adequate decisions is flawed by assumptions and practical problems that, even if the price signal is correct, do not provide adequate decisions. Examples are the assumptions that money is worth more today than tomorrow (discounting), or the substitutability of resources [14, 12]. In general, there is no consideration of the financial impact of eventual resource limitations, when discounting methodologies are utilised. The discounting concept as implemented in practice conflicts with the fundamental principle that the economy should function as to be indefinitely sustainable. Another assumption common to standard economics is that the substitutability of resources can be based on monetary value, which in turn reflects scarcity. The substitution assumption, however, is very questionable; some mineral resources may prove critical for future technologies.

of industrial ecology. The development and management of eco-industrial parks, however, is not well understood, despite of the many studies on Kalundborg and other eco-industrial parks. A detailed mechanism or recipe, by which the conditions for the development of the required industrial symbiosis can be achieved, remains to be worked out [97]. The symbiotic relations in eco-industrial parks are not invented, but tend to develop in a complex, organic way. Because of the many different actors, factors and processes involved, the steering of this process is complex, and involves many trade-offs. In addition to the technical and environmental aspects at process level, many other aspects play important roles. These include an obvious need for long-term co-operation and planning, e.g. to address the risk of loosing a critical supply in case one of the existing plants changes feedstock, or closes. The development also calls for a disclosure of relevant technical information, but then proprietary information could become available to competitors [97]. It appears that a high level of organization is required to ensure successful co-operation. Gertler [98] gives a comprehensive overview of the conditions for creating inter-company by-product exchanges based on Kalundborg. These include the regulatory changes needed, and the organizational options for creating and managing such changes. Other attempts to draw up recipes for the development of eco-industrial parks are given by Côté [92, 99] and Lowe [100]. Once these eco-industrial parks have been developed, they need continuous maintenance and management. While ecosystems 'unconsciously' and continuously adapt to their surroundings, the high level of organization and the strongly integrated designs of eco-industrial parks could lead to a lock-in of undesired technologies, continued reliance on toxic compounds or overall a limited flexibility [71, 101, 102, 13]. Tibbs [103] already recognized the need for a design for flexibility. He proposes that the concept of a learning organization can be used in the design of an eco-industrial park. One of the characteristics of a learning system is that one has the ease of making and breaking connections as conditions change. Therefore, internal technological choices and transactional arrangements must continuously be compared to the external competitiveness of the system as whole [97]. It can thus be easily seen that understanding the technical systems that largely determine the technological choices and transactional arrangements is a condition to develop and maintain eco-industrial parks. Similarly, the shift in regulation endpoint from localized reduction of (usually human) risk implicit in much environmental policy and legislation to date, to a goal of global economic and environmental sustainability also involves controlling the highly complex technical infrastructure (see also Chapter 4). Closing the material cycles, for example, involves the co-ordination of processes that can be dispersed worldwide [104]. It thus can be seen that, adopting the systems perspective of industrial ecology carries with it a fundamental shift in focus from simple to complex systems. Allenby [14] summarizes the fundamental difference between simple and complex systems as follows: Simple systems are intuitively "understandable". In contrast, many aspects of complex systems are difficult and counterintuitive[8], and frequently are illustrated only by the behaviour of properly constructed quantitative models. Industrial ecology calls for the co-ordination of processes that operate at different time scales and spatial scales. The principle of mass conservation provides a tool to describe processes across different time scales and spatial scales. Durchin and Hertwich [105] therefore consider the descriptive approaches, SFA in particular, as the unifying core of industrial ecology. The descriptive approaches are thus important for the prescriptive approaches for two reasons. First, they represent the experience in the quantitative modelling of the complex patterns of material and energy flows, and in the conversion of these patterns into quantitative support for the formulation and evaluation of options for decision-makers. Secondly, they should provide the context to co-ordinate the efforts of the different prescriptive approaches and as such

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[8] Because complex systems typically operate far from equilibrium, they often have no causal or linear relationships, they exhibit discontinuities, thresholds etc.

provide a unifying core for industrial ecology.

2.5.2 Descriptive approaches

The descriptive approaches involve the analysis of the flows of materials and energy in industrial and consumer activities, and of the effect of these flows on the environment. Here a distinction can be made between studies that are performed in physical terms (resource studies) or in monetary terms (social and economic studies).

Strength

The fundamental importance of identifying and tracing physical flows of materials and energy has been recognized for decades. Descriptive approaches provide snapshots of parts of the physical economy. They enable tracing environmental problems to their origins, assist in formulating policy or design alternatives, and predicting future bottlenecks towards sustainable global economy. Moreover, descriptive approaches can assist prescriptive approaches by providing a connection of the flows of mass and energy to social and environmental costs. Based on different goals, concepts, time and spatial scales and target questions, Figure 2.2 shows that various methods have developed in industrial ecology. Material flow analysis (MFA) emerged as one of the primary methodological frameworks [106]. All of these approaches are based on mass and energy balances of a certain part of the flows and processes of the global economy, associated with individual product and processes or national to global economies. The development of a paradigm embracing the identification and tracing physical flows of materials and energy has been slow, and still lacks a clearly defined methodology [107]. The methods differ in how they present subsystems of global physical economy; for example which resolution they use to describe physical economy, or how they consider the dynamics of the system. The inputs and outputs of the inventory in life cycle analysis (LCA) generally lack a time dimension ; they are amounts per se, or more precisely per functional unit of the product (or process) under investigation [41]. In contrast, substance flow analysis (SFA) investigates the processes, flows and accumulations of certain materials over a certain period of time. Bringezu and Moriguchi [108] and Daniels and Moore [106] attempted to classify the different methods based on their subject, i.e. which part of the global economy is described by the approaches. Daniels and Moore distinguish five families of methods based on the MFA framework:

- Macro-Bulk/Material Flow Analysis (Macro-BFA) investigates the total economic activity in a region of all material groups.
- Partial Macro-MFA differs from Macro-BFA in that it investigates only one substance, or material group.
- Meso-MFA considers all material groups, but focus at a single sector or activity field
- Micro-MFA, considers the same as Meso-MFA, but at micro scale (one or only a few products or enterprises)
- MFA-related methods include the reaming methods that consider the total economic activity of region or a process.

Bringezu and Moriguchi [108] distinguish two categories of methods: MFA type I and II . Each category is divided into three subcategories, a. b, and c. The two categories represent opposite focuses: type I focuses on (a) substances, (b) materials and (c) products within firms, sectors and regions, and type II on (a) firms, (b) sectors and (c) regions associated with substances materials and products. The two classifications of MFA (and MFA related approaches) are summarized in Table 2.1.

Weaknesses

The strength of industrial ecology lies in its descriptions of the material world. Life cycle analysis accounts for most articles in the Journal of Industrial Ecology, and most sessions at professional meetings [105]. There are still substantial challenges in achieving conceptual and operational linkages between the physical balances and the formulation and evaluation of options for key decision-makers. One of the challenges for the descriptive approaches is the 'impact assessment' step, which involves evaluating the significance of hundreds of inventory items in terms of a small number of indicators [109]. Environmental stressors may be aggregated into impact categories or themes such as climate change, ozone depletion, human toxicity, ecosystem toxicity, and biotic resource depletion. Alternatively, impact can be reported in terms of damages, like years of life lost or an estimate of the monetary cost of damage (see Section 3.5).

Nevertheless, advancing sustainability through a deliberate and rational eco-design of the industrial activities would benefit greatly from properly constructed quantitative models that can support and connect the different prescriptive efforts, and thus assist in their co-ordination. The descriptive material flow analysis approaches available can support prescriptive approaches. Many prescriptive approaches rely heavily on the description of transformations and flows of materials and energy, such as MFA, LCA , Input-Output analysis, economic accounting etc. The LCA profile of a product can be used for comparison against competing products, or for suggesting ways to improve a particular product design. The LCA profiles can also be used to justify the eco-labelling of product designs. MFA and SFA are helpful in identifying defects, inefficiencies or leaks in processes or systems of processes. When applied to production processes it serves as a basis for cleaner production or pollution prevention to remedy those problems by process innovations. When applied to systems of processes, it serves a basis of industrial policy. A description of the processes and flows to address IE strategies, such as dematerialization, or closing the material cycles, requires both scope and depth. Realizing these strategies requires detailed understanding of the capabilities of the underlying material and energy processing systems. To enable continued cycling of materials, obsolete products, and residues must be transformed into resources of a comparable quality as the original resources. Available knowledge, process operation and thermodynamics restrict the range of material combinations that can be transformed into new resources and products, and differ with their geographical distribution. Policy, product and process designs based on environmental considerations need to consider these (technological) constraints. However, often holistic approaches, such as industrial ecology, concentrate on scope and are perceived by engineers to suffer from lack-of-content [25]. Even highly detailed studies on the flow of substances, such as the collection of articles tracing stocks and flows of copper in Europe by Graedel and colleagues [110], overlook the complexity of the industrial (metal) metabolism. Also in authoritative Industrial Ecology handbooks, including Graedel and Allenby [12], Ayres and Ayres [11], and Ayres and Ayres [15], the industrial process routes are often oversimplified, or many interconnectivities and interdependencies are neglected [111, 16, 7, 23]. Consequently, many real impediments to closing the material cycles and other strategies may be overlooked. The various descriptive methods were developed for specific goals, concepts, time and spatial scales, rather than providing an integrated description of the flows and transformations and

Table 2.1: Summary of different MFA (and MFA related approaches) based on system boundary and application (after Bringezu and Moriguchi [108], Daniels and Moore [106])

Classification of the different MFA and MFA related approaches according to Daniels and Moore

MFA classification	Economic System investigated	Substances investigated	Examples approaches
Macro-BFA	Total economic activity/region	All material groups	Bulk internal flow MFA (MFA-BIF), Total material requirement and domestic output (TMRO), Physical Input/Output tables (PIOT)
Partial Macro-MFA	Total economic activity/region	One substance, or material group	Substance flow analysis (SFA)
Meso-MFA	Sector, activity field	All material groups	Product chain analysis, material flow balance studies focussed on specific sectors.
Micro-MFA	One/few products, enterprise	All material groups	Material intensity per unit service (MIPS), Life cycle analysis (LCA), Company-level MFA
MFA-related	Total economic activity/region (ES, EFA) Process (SPI)	All material groups	Environmental space (ES), Ecological footprint (EFA), Sustainable process index (SPI)

Classification of the different MFA and MFA related approaches according to Bringezu and Moriguchi

MFA classification	Focus	Examples	Remarks
MFA type I: focuses on substances materials and products within firms, sectors and regions	a Substances	Cd, Cl, Pb	Usually coined Substance Flow Analysis (SFA)
	b Materials	wooden products, energy carriers, biomass, plastics	This kind of study is related to Ic and IIb
	c Products	diapers, batteries	Usually classified as LCA
MFA type II: focuses on firms, sectors and regions associated with substances and products	a Firms	single plants, medium and large companies	Usually related to environmental management, and not classified as MFA
	b Sectors	production sectors, chemical industry, construction	When the analysis comprise all sectors of regional or national economy closely related to IIc, if it comprises of one sector in detail to Ib.
	c Regions	total/main throughput, mass flow balance, TMR	The scope varies from cities, to regions (e.g. Rhine basin), and national economics

their impacts on the environment across various levels in the physical economy. As a consequence, each method is a compromise between scope and depth. As shown in Figure 2.2 and Table 2.1, the different MFA approaches are complementary. Each approach addresses different aspects of the overall objective, and can contribute to the understanding and improvement of the overall metabolism at various levels. Many researchers in the field observe a methodological convergence in the current trends in research and modelling of environment related flows in the physical economy [112, 113, 114, 115, 116, 117, 118, 119, 106, 120]. Such convergence could yield significant benefits with respect to the underlying data collection, access and conformity, and analytical conformity. It enables studies at a high level of aggregation to build on studies describing the underlying systems, or vice versa. The combination of the methods can thus provide both scope and depth. This is crucial to address industrial ecology strategies that often operate at multiple levels, and go beyond the scope of the tools individually.

2.6 The promise of Industrial Ecology

Industrial ecology is sometimes regarded as the science of sustainability. Its promise is a roadmap for a deliberate and rational approach of sustainability, given continued economic, cultural, and technological evolution. This section investigates whether the concept (Section 2.6.1) and tools (Section 2.6.2) make up for that promise.

2.6.1 The concept of industrial ecology

Sections 2.1 and 2.2 showed that sustainability is a complex concept with many different aspects. A first question is therefore to what extent the implementation of industrial ecology leads to sustainability. Ehrenfeld [54] distinguishes three categories of strategies for sustainability, each reflecting different aspects of sustainability: Rationalistic strategies are based on the historic 'rational' ways of thinking and reflect dominant basic ideologies such as competitive markets, utilitarian and optimism in technology. Naturalistic strategies are based on models of natural systems and their limits in supporting human economic activities. Humanistic strategies emphasize the 'flourishing' aspect of sustainability. Industrial ecology falls into the naturalistic category. It uses a biological analogy to describe and analyze industrial systems. It is based on models of natural systems that are thought to be the best or perhaps the only examples of sustainable systems. Nature consists of ecosystems: carefully balanced, and integrated closed loop systems of co-operating organisms and their physical surroundings. These ecosystems have certain properties that can be applied to the industrial activities to make them more sustainable. Although the analogy between the industrial ecosystem concept and the biological system is not perfect, much could be gained if the industrial system were to mimic the best features of the biological analogy (Erkman et al. [68], after Frosch and Gallopoulos [121]). The objective of a deliberate and rational approach of sustainability[9] reflects that industrial ecology may contain rationalistic elements as well. Graedel and Allenby [12] explain that the words deliberately and rationally indicate that the intent of the field of industrial ecology is to provide the technological and scientific basis for a considered path towards global sustainability, in contrast to unplanned, precipitous and potentially quite costly and disastrous alternatives. Extended producer responsibility, resource or eco-efficiency, the precautionary principle and product-service systems are recent examples of rationalistic

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[9] Industrial ecology is the means by which humanity can deliberately and rationally approach a desirable carrying capacity, given continued economic, cultural, and technological evolution. See Section 2.3.

strategies [54] but are also important strategies in industrial ecology. A distinctive characteristic of industrial ecology is that it puts rationalistic strategies of reductionist science and linear short term and obvious causality by more systems-based, into context of comprehensive naturalistic approaches. Desirable in the objective of industrial ecology indicates that, given the potential for different technologies, cultures and forms of economic organization, a number of sustainable states may exist. It thus becomes a human responsibility to choose among them, and act so as to approach the desired state that otherwise would not have occurred. Industrial ecology strives to be objective, not normative. Thus where cultural, political or psychological issues arise in industrial ecology, they are evaluated as objective dimensions of the problem [40]. Dutchin and Hertwich [105] describe it as follows:

> *"Industrial Ecology aims to provide information for decision makers, especially in a corporate setting, but also in public institutions and households. It has until now not embraced systematic approach to studying the economic, social and psychological aspects of decision-making. While Industrial Ecology is a truly interdisciplinary enterprise, the concerns of social scientists are addressed only on its margins."*

Apart from converting products to services strategies, industrial ecology does not really address the 'flourishing' aspect of sustainability (see Ehrenfeld [54]) . Industrial ecology only involves some aspects of sustainability. It focuses mainly on industrial activities, and seeks technological evolution based on ecosystems models to keep industrial activity within environmental constraints. Industrial ecology optimizes only part of the system. As the concept of a sustainable subsystem in an unsustainable global system is a fundamental oxymoron, implementation of industrial ecology alone can not lead to sustainability. Industrial ecology is, rather than a roadmap to sustainability, a critical step towards sustainability that may buy the time necessary for the cultural/social evolution.

2.6.2 Tools

Allenby [14] suggested that because of the systemic character of sustainability , the western concepts of reductionist science and linear short term and obvious causality will have to be augmented by more systems-based, comprehensive approaches to develop the appropriate tools to approach sustainability. Industrial ecology provides for at least part of the context that would allow for the development of these tools. The second question is to what extent the available set of tools enables the implementation of industrial ecology, and advance towards sustainability. In potential, industrial ecology is a systemic framework that connects environmental problems, issues and analyses at different scales and a context for adapting and applying existing methods and tools, and for creating new ones [13]. In addition, industrial ecology could provide for a multidisciplinary 'forum' or a common language to overcome conceptual and professional isolation, and differences in interpretation. The strength of industrial ecology is that is provides a context for analysing the industrial economy at different levels of aggregation, from individual processes and products to the global material cycles. This ambitious domain of application is at the same time also the weakness of industrial ecology. The literature on industrial ecology is a cluster of more or less interrelated concepts, tools, metaphors and exemplary applications and objectives [78], and has no clear demarcation of the field. Each of these concepts, studies and tools is based on different interpretations of the content of the field, and addresses different problems, which in turn results in different sets of system components and levels of aggregation used. The latter appears common also in ecological studies, where different 'ecosystems' can be chosen depending on the issue addressed. The current vagueness of the concept opens the way for potential misuse as marketing or public relation tool [83]. It allows for trivializing the problem by emphasizing small, internal components of the industry rather than its large, more basic interaction with the environment [122]. Or it loses its content as an analytical or prescriptive tool by including so many details that no realistic solution can be found [123]. Boon and Baas [123] promote a choice of optimization domain of industrial ecology; this could ease its acceptance as an analytical tool. However, sustainability is an emergent characteristic of the global economy as a whole . A too narrow choice of a domain may limit the set of problems and solutions visible, or lead to suboptimum or unsustainable solutions. The knowledge of the system to understand and guide industrial systems towards sustainability must be obtained through analyses and co-ordination of activities across different levels of aggregation [124, 121, 101, 125, 23][10]. Rather than a choice of optimization domain, Lifset and Graedel [78] stressed the importance of understanding the "endeavours that comprise industrial ecology and how those endeavours interrelate to each other". In a recent editorial of the Journal of Industrial Ecology, Allen [126] discussed the need for a set of core principles and tools. He also concluded that it is time to "begin to more clearly articulate our field, its principles, its tools, and, possibly, its values". Lifset and Graedel [78] do not consider the current looseness as a fatal flaw in an emerging field, but rather as an opportunity for creativity and constructive discourse, and as a challenge. However, it is challenge that must be addressed to deliberately co-ordinate industrial ecology endeavours to accomplish the desired (technical) evolution. Ehrenfeld [127] once coined industrial ecology a technological approach to sustainability. The methodological convergence in the current trends in research and modelling of environment related flows in the physical economy appears a first, but critical step. For the development of a 'objective' framework connecting the prescriptive studies at various system levels, the different descriptive approaches must be connected as well, i.e. at least able to use each others data and results, and/or more advanced industrial ecology models must be developed span various system levels. Industrial ecologist should particularly take care of a sufficient 'technological' depth in these models. The patterns and transformations of mass (and energy) flows, upon which all the model approaches are based, are largely shaped by the technological system. To date, but most of the descriptive studies oversimplified this system.

2.7 Summary

In the last decades, sustainable development has become the cornerstone of environmental policy, and a leading principle for resource management. Sustainability, the continued welfare of human and other life on earth, is an emerging system property. The designation refers to the fact that sustainability is a property of the system as a whole and that one can not know that the system is sustainable until in fact sustainability has been achieved. Sustainability is not a specific system configuration that can be accomplished, but rather a property that emerges from the continuous co-evolution of human and natural systems. As a consequence the concept of sustainability provides little assistance for decision making in specific cases. Industrial ecology is an ecological or systems approach that focuses on a part of sustainability. It can make the concept of sustainability applicable to decision-making. Based on sustainable examples in nature, ecosystems, it aims to achieve a deliberate (r)evolution of industrial activities within the boundaries set forth by natural systems they are founded on. Industrial ecology thus determines the industrial conditions for sustainability. Its implementation can buy time for the necessary societal evolution. This deliberate development of industrial

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[10] IE begins with process optimization [121], but must go "beyond individual company or plant boundaries to seek improvements in the performance of larger systems" [124].

systems towards sustainability requires (i) the co-ordination of industrial activities mutually, and with the other activities in the resource cycles, and therefore (ii) the support of decision-making across various organizational levels that influence industrial activities. Two elements can be distinguished in industrial ecology approach: descriptive and prescriptive elements. The descriptive element describes the industrial system at and across system levels. The prescriptive element aims to stimulate decision-making based on considerations of sustainability. However, different prescriptive elements are not always complementary, and can be conflicting. For the realization of the objective, through co-ordination of decision-making across system levels, descriptive approaches should be able link the different prescriptive efforts by showing their effect consistently at the various levels of the industrial system. This can be realized by proper modelling of the underlying technological subsystems, and convergence of the different descriptive models that generally address the higher system levels. Only if industrial ecology models can build on the results of models of underlying systems (and the other way round), a consistent picture of the influence of different effort can be obtained.

Chapter 3

A description of the metal cycles

The systemic perspective of industrial ecology calls for a shift from dealing with isolated, relatively simple systems to managing complex, interdependent systems. Quantitative models are essential in acquiring insight in the behaviour of such systems, and thus for advancing industrial ecology. The interconnected metal cycles, the metal production and recovery system in particular, form an example of such a complex system. Industrial ecology inventories have oversimplified metal production system systems, and as a consequence cannot to be expected to invoke improvement in these systems. This chapter presents a description of the metabolic routes through society as a basis for quantitative modelling, focusing on metal production and recycling. Most metal and material cycles are rather complex and interconnected, which calls for a suitable architecture before they can be simulated satisfactorily. How can interdependent networks of processes be mapped and characterized? What level of resolution is necessary to characterize the material cycles. What type of information is necessary and what information is available? The chapter starts with a general introduction on the metals production (Sections 3.1 and 3.2), the suitable modelling architecture (Section 3.3) and the availability of data (Section 3.4). Finally, the implications of this modelling/inventory approach are discussed with respect to the descriptive approaches of industrial ecology and the quantification of the physical economy (Section 3.5).

3.1 Metal resource cycles

The systemic perspective of industrial ecology calls for a shift from dealing with isolated, relatively simple systems to managing complex, interdependent systems. Quantitative models are essential in acquiring insight in the behaviour of such systems, and for advancing industrial ecology. Ideally, such models must be able to visualize the behaviour of the systems, and link the behaviour to environmental issues. This involves two stages: first, one must make a mathematical reconstruction to predict flows and transformations across system levels, as well as the emissions in and extractions from the environment caused by flows and transformations; second, one needs to translate these emissions and extractions into impacts to the environment, which are understandable to decision-makers. In this chapter, the quantitative description of the systems of the different interdependent processes involved in production and recycling of eleven metals is presented.

A resource cycle perspective is used, which also a common way of abstraction in ecology and biology. In industrial ecology literature, however, often a life cycle perspective is used. Figure 3.1 shows the life cycle of a car. Because for the production, use and recycle many

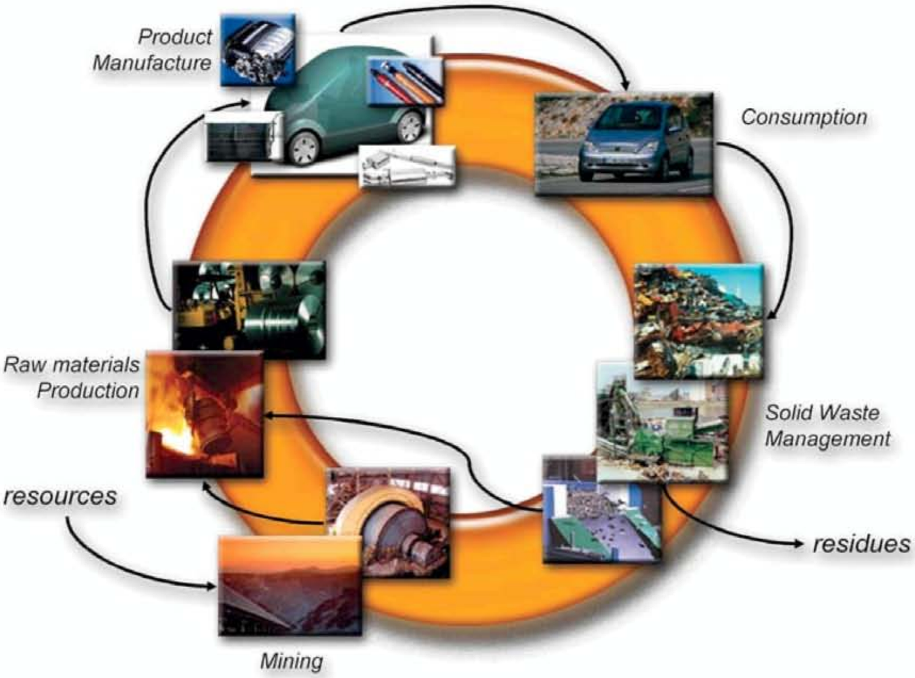

Figure 3.1: The life cycle of a car: natural resources (e.g. ores, oil) are mined/extracted, concentrated, and processed into raw materials (e.g. metals, plastics). The car components are made from these raw materials and combined in the manufacture of the end-product. After its useful life the car is dismantled, shredded and separated into new resources that complement primary resources (after Reuter [52]).

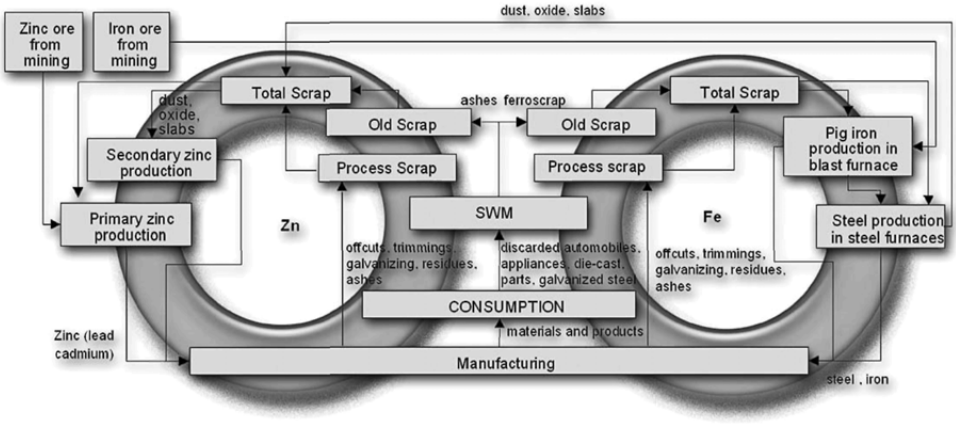

Figure 3.2: The coupling of the iron and zinc resource cycles through their combination in cars; zinc from the galvanized steel parts is separated in the steel furnace and concentrated in the Waelz kiln to be refined to a grade of zinc that can be used again for galvanizing.

different materials are involved, its production connects the resource cycles of these materials (see also Chapter 1 and 4). For example the zinc en steel cycles as illustrated in Figure 3.2. These interconnected industrial metal resource cycles - consisting of the metal mining, production, manufacture and recycling systems - appear an excellent case study to investigate the possibility of capturing complex systems in quantitative models for two reasons. First, industrial ecology attempts to design and manage industrial systems as ecosystems through adaptation of typical ecosystem features including, minimal use of resources and minimal production of wastes by cascading the use of resources and energy. Because the industrial metal systems have been around for a long time, most of the metal processing technologies are well developed, and the "industrial ecosystem" is well established. The next section, which discusses the metal production from an industrial ecological perspective, will show metal production systems have already largely adapted these and other typical ecosystem features (e.g. a certain "resilience" to "environmental perturbation" through interdependence and diversity of its components and diversity in its material flow patterns). Second, metals constitute a significant part of the industrial materials consumption and are thus important resources in absolute terms. Moreover, metals have been catalyst for the development of biological life and in the development of our current civilization. Today metals have invaded virtually all aspects of the Western lifestyle. Third, industrial ecologist perceive the metal production processes as an important source of pollution, but simultaneous recognize their importance for present industrial societies: Sagar and Frosch [101] for example argue that metals are unlikely to be displaced by other materials to a significant extent in the near future because other materials suffer from constraints that will continue to make metals useful: polymers, for example, can not routinely offer the stiffness, strength, and heat resistance that metals can, and ceramics do not offer the same toughness or impact resistance.

3.2 An introduction to metal production

To meet the demand for metals, enormous quantities of metal ores are extracted from the earth's crust each year. Metal ores are minerals that contain a relatively high percentage of one or more metals, but typically contain many other elements as well (Figure 3.3). The production of refined metals from the ores involves the removal and processing of much more materials than the amount of refined metal eventually produced. A large amount of the extra material is removed at the mining sites as gangue or overburden. Even after this concentration process, the ores shipped to the metal production facilities are still very heterogeneous in nature; the exact composition of the ores varies with mining location. Secondary raw materials are very heterogeneous in nature as well and their composition changes with location and time.

3.2.1 Interdependence

Ecosystems tend to develop towards increased diversity and interdependence. Similarly, the metal system has developed towards increased diversity and interdependence in order to maximize productivity and economic efficiency. The different ore compositions and effect of impurities (i.e. the other metals or "co-elements") in ores on the metallurgy shaped the development of the industrial infrastructure for metals processing. Among others due to the slow development of metallurgical processes, their long lead times and economic life spans, the metal production network developed as an interconnected and integrated system that incorporates multiple production routes for a spectrum of metals. More often than not, the production or recovery of a single metal is related to or dependent on the generation or recovery of other metals. Diversity in and interconnectivity between metallurgical processes are key elements in the

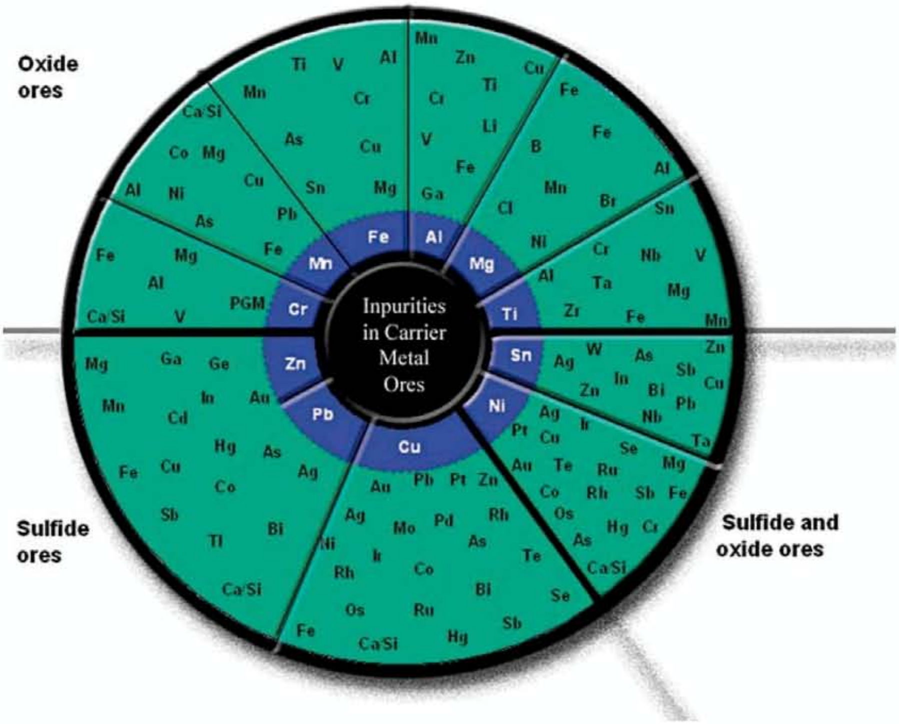

Figure 3.3: The impurities in the ores of different base metals. The bold radial lines divide the metals into three groups, sulphide ore, oxide ore, and a mixture of sulphide and oxide ores, whereas the lighter radial lines separate the individual metals. The light radial line odes not separate zinc and lead ores completely because these metals are typically mined together.

development of the metallurgical capacity to exploit the economic benefits of the impurities and to cope with increasing environmental pressure.

To illustrate this, the development of lead and zinc production is taken as an example. In order to realize the potential economic importance of impurities and meet the increasing environmental pressure, research and development integrated the processes of copper production with those of lead and zinc, and connected the processes to those of among others silver, bismuth, tin and the platinum group metals (PGMs). The recovery of these metals is complex, as most of the elements must be circulated between two or more production circuits (nickel and gold, see Figure 3.12) before they are concentrated enough to make their extraction possible, and their recovery as a metal profitable. In addition to recoverable elements, there are a number of other elements that must be separated to allow production of high-grade metals. These elements are usually separated in the slag or off-gas treatment system, at one stage or another in the web of processes . As a consequence, the production of these metals is so interdependent that they can hardly be considered separately. In zinc processing, for example, two complementary process routes co-exist (Figure 3.4). On the one hand, hydrometallurgical zinc production (Figure 3.5) offers the lowest operating costs, but it can only be employed for very specific types of zinc ores. On the other hand however, one can employ a variety of primary and secondary raw materials in pyrometallurgical zinc production, and recovery of by-products and residues is feasible [128]. The combination of these two routes can be more effective in minimizing the environmental impacts of the metal production system, than either one individually.

In case a feedstock contains iron compounds for example, the hydrometallurgical route would generate a hazardous iron residue in the neutral leach process. Processing the iron-containing feed in the pyrometallurgical route, would lead to the use of extra fossil fuel (cokes, coal etc.) and to more emissions compared to the hydrometallurgical route. In the combination, however, the hazardous residue that originates from hydrometallurgical zinc processing can be treated via the pyrometallurgical route. More specifically, the pyrometallurgical Waelz kiln or Imperial Smelter Furnace (ISF) can be integrated into the hydrometallurgical route and reduce zinc ferrite to form zinc oxide and iron [129].

For instance, at Ruhr-Zink about 30 different concentrates are roasted and subsequently leached for zinc dissolution and iron removal (Figure 3.6). After purification of the zinc containing solution zinc is recovered in the electrowinning plant. The leaching process at Ruhr-Zink passed through most of different technological developments in the above figure since its start up (1968). Iron was separated from the solution initially as Jarosite , later as Hematite. Pressure leaching was applied for a while to increase the production capacity. Today Ruhr-Zinc is back to a rather classical type of process, which in the midterm might turn out to be among the most modern and future oriented technologies [128]. While most of the world wide hydrometallurgical plants for zinc recovery still precipitate the iron from the leaching solution as jarosite which is dumped in ponds or caves, Ruhr-Zink stops its leaching operation before the iron content of the concentrate is dissolved thus producing a Zinc Ion Concentrate (ZIC) which is shipped to an Imperial Smelting facility for further recovery of the valuable elements Zn, Pb and Ag. The iron in the Ruhr-Zinc process is bound in the stable slag of the IS-furnace, which can be used for road construction. Figure 3.6 shows that in addition to the primary concentrates, Ruhr-Zink also processes an increasing amount of secondary Waelz oxides.

Another example of successful integration is the zinc-lead Plant at Portovesme in Italy (Sardinia) that originally consisted of a sintering facility, an Imperial Smelter furnace, two additional Waelz kiln to pre-treat local ores, a small rotary kiln for the production of clinker, a cadmium plant, a zinc refinery and a sulphuric acid plant. The addition of an electrolytic

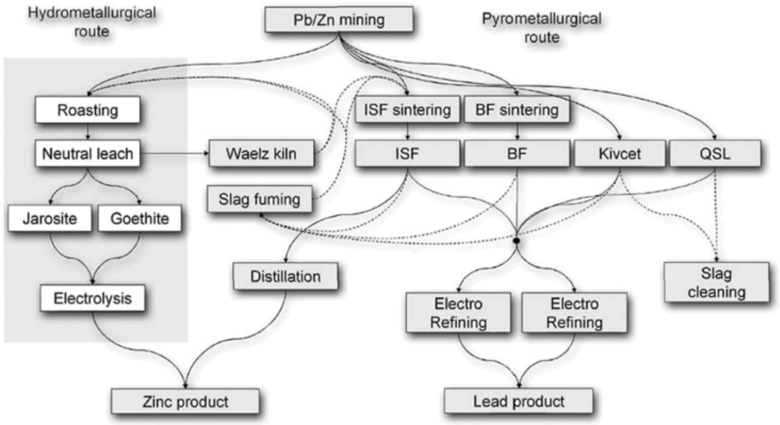

Figure 3.4: Simplified flow chart of the interconnected primary zinc and lead metal production routes. Legends: ISF = Imperial Smelting Furnace, BF= Blast Furnace, Neutral leach= Neutral Leach Process, KIVCET = KIVCET Furnace, QSL=QSL Furnace, Jarosite = Jarosite Precipitation Process, Goethite = Goethite precipitation Process [7]

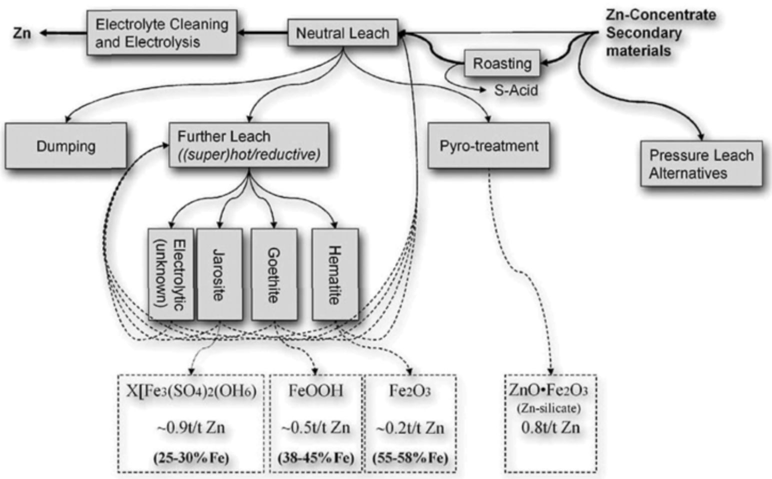

Figure 3.5: Process options for iron removal in hydrometallurgical zinc route [128]

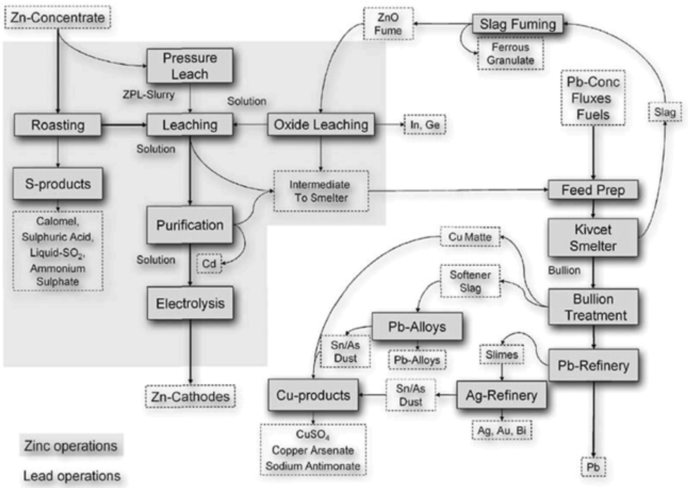

Figure 3.6: Schematic flowsheet of the Ruhr-Zink GmbH zinc plant in Germany [130]

zinc plant (1985) and a Kivcet smelter (1987) fully integrated the production of lead and zinc (Figure 3.7). This did not only result in a large production capacity for lead and zinc, but also in an optimum metal recovery and minimized amount of waste materials due to the internal cycles of flue dusts, residues, and other streams [128].

3.2.2 Resilience

Ecological systems must continuously adapt to changes in their surroundings, or else they vanish by ecosystem transformation, or ecological succession. Ecosystems are resilient to changes in their environment through continuous changes in populations of all the organisms in ecosystems, and their adaptation on the longer run. In case, perturbations in the environment are larger than certain ecological thresholds, ecosystems may collapse to be replaced or develop into new ecosystems with a different community structure, often better adapted to the perturbations. Odum [86], Lovelock [88, 89] and others saw the development of ecosystems as a "strategy" of increased control of the physical environment toward achieving a homeostasis, which provides maximum protection from environmental perturbation. Increased biodiversity and pattern diversity are characteristic for the homeostasis-state. The industrial diversity and diversity in production patterns also provide for resilience and flexibility in the production of metals. Each metal process has a different knowledge base (metallurgical, technological, fundamental and theoretical expertise), and technological capacity to deal with different concentrations of metal, impurities and valuable elements. Different ways of interconnection of the processes provide a flexibility to deal with concentrates of different composition and improved residue processing. Waelz kilns can process a wide range of raw materials with as lows as 25% (or even 15%) zinc content, among others hydrometallurgical leach residues, into suitable zinc concentrates of around 45% zinc content. Figure 3.8 shows the options for processing of the Waelz oxide and slag. Dependent on the raw materials used, and/or the demand for (zinc) concentrates, the slag and oxide can follow different routes to refined zinc, iron/steel and other metals.

The primary product of the Waelz kiln is an impure grade of zinc oxide (Figure 3.8). The zinc oxide is usually calcined in a rotary kiln to produce clinker oxide, to make it suitable as raw material for the production of zinc metal and/or chemicals. Calcination is operated to volatilize Pb to PbO and also to remove other impurities such as Cl and F. The Waelz oxide can also be used as a raw material for the hydrometallurgical zinc process, but then the chlorides that contaminate the Waelz oxide must be removed by leaching (see also Figure 3.6). The iron compounds in the feed are removed in the slag (the secondary product of the Waelz kiln) as FeO or to some extent iron metal. Other principal components of the slag are CaO and SiO_2. The slag is for instance reused for road construction, as fertilizers or as a base for the sinter mix in iron-making. Figure 3.4 is a simplification; it shows the main production routes for zinc. The diversity and partial overlap in process functions between different metallurgical processes allow a certain flexibility in the zinc-lead production routes. Besides treatment in an ISF or Waelz kiln, hydrometallurgical residues can also be treated in a Kivcet smelter. Figure 3.9 shows the fully integrated processing of lead and zinc at the Trail facility. Iron and lead residues created in the zinc operations ("intermediates to smelter") are processed in the lead operation and comprise nearly half of the total feed of the Kivcet furnace. Zinc-rich smelter fume is fed back to zinc operation and makes up about 15% of the total feed. Sulphur dioxide off-gases from the roasting process are fed to the sulphur gas handling plants in the zinc operation and waste water streams from both lead and zinc operations are treated in the effluent treatment plant.

The combined zinc and lead production can also recover indium, germanium, silver, gold,

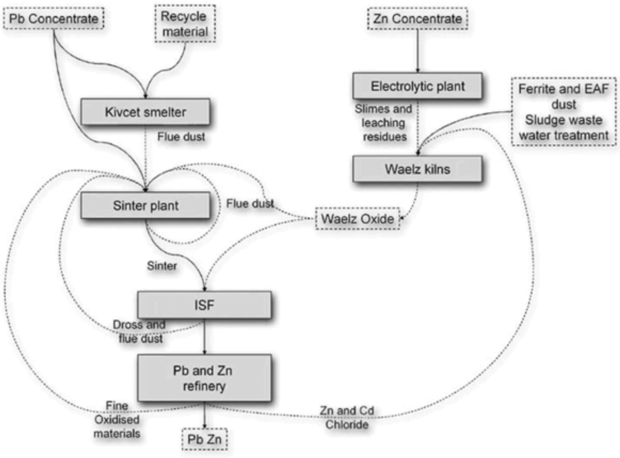

Figure 3.7: Schematic flowsheet of the residue processing at Glencore International AG zinc-lead Plant in Portovesme, Italy [128]

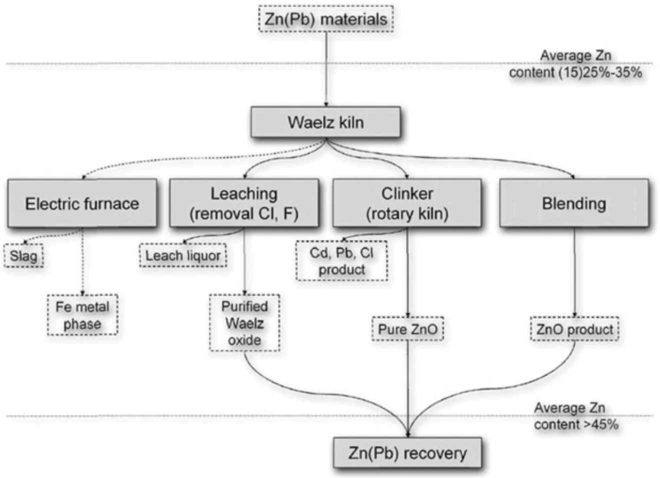

Figure 3.8: Process options for Waelz oxide and slag processing [128]: the Waelz slag can be applied for dike building etc. without or with limited further processing such as the removal of iron

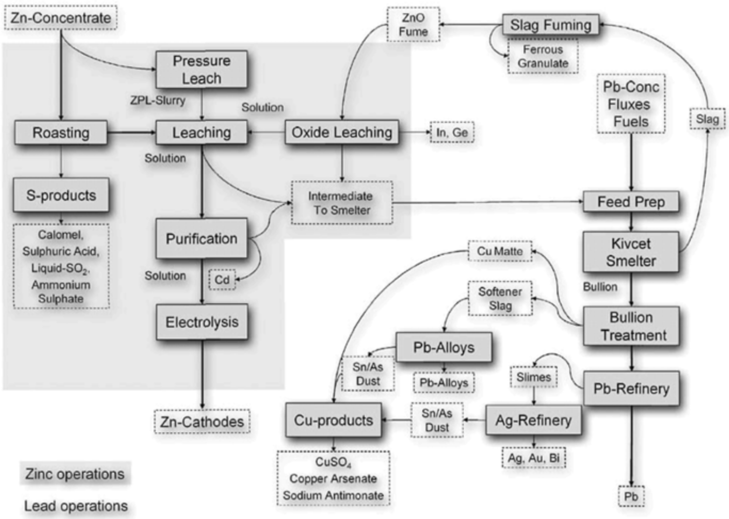

Figure 3.9: Schematic flowsheet of the Cominco zinc-lead Plant at Trail in Canada [131]

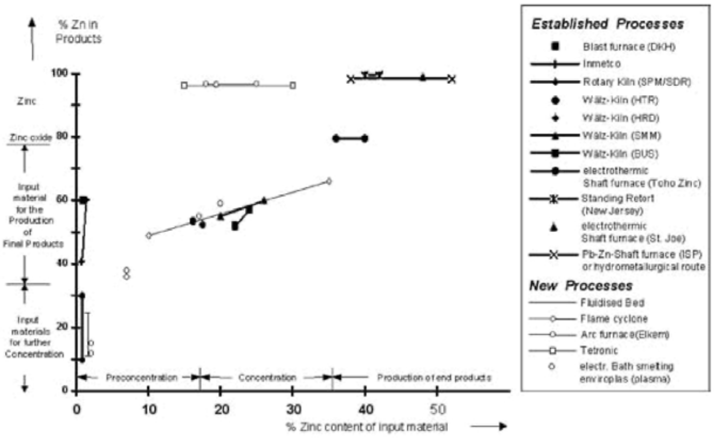

Figure 3.10: Processing specifications for zinc - overview [132] (depicts feed and product concentrations of zinc processes)

bismuth, arsenic metal, and copper products. Indium, germanium are recovered in an oxide leaching step, which pre-treats the zinc oxide fumes from the lead operations. Pressure leaching is integrated in the zinc operations, recovering elemental sulphur. The leach residues are a secondary sulphur raw material for the lead smelter. The cement from the purification of the zinc bearing solution is further treated to recover cadmium and a copper cake; zinc is produced in an electrolytic operation. The lead operations of the Trail plant treat zinc residues, lead concentrates, recycled batteries and lead bullion to produce silver, gold, bismuth, arsenic metal, copper sulphate, copper arsenate, sodium antimonite.

Because of the many different processes available for zinc production from concentrates with varying zinc concentrations (Figure 3.10) and impurity levels, the integrated metal production circuits also provide a limited flexibility to deal with varying concentration of the bulk metal. For zinc, for example, no processes are currently available for the processing of materials that contain 4-8% Zn. Figure 3.10 shows the available technology to process raw materials of different input concentrations of zinc (x-axis). On the y-axis one can read the produced zinc concentration of that technology. The figure illustrates that a combination of processes allows the processing of most concentrations of zinc. Dependent on the concentration and composition of the concentrate different routes for metal production are available. Zinc concentrates of 2% Zn can be processed in Rotary kiln to 10-30%, further concentrated in a Waelz kiln to 50-60% and finally refined to zinc metal in the Imperial Smelting process (ISP) or the hydrometallurgical route, for example. Above zinc concentration of 35%, zinc metal (100%) can be produced in one step. Usually the primary concentrates for zinc metal production lie around 55%. At system level, this means that for a continually changing feedstock, the geographical routes from (primary or secondary) raw material to metal can not be fixed, but must also be subject to change.

3.2.3 Tacit Knowledge

It can be easily seen there is not a single technology available that can produce and recycle all metals. Rather the metallurgical system consists of large number of different processes that are interdependent and must co-operate and compete to produce metals from a wide-ranging and changing set of raw materials[1] . In an industrial ecology perspective, the metal ecology can be seen as an evolving system made up of (semi-) autonomous "organisms", that have partially overlapping functionalities, and self-organize into many higher-level structures such as production circuits, or sectors in a bottom-up fashion [133].These interconnected networks are examples of industrial ecology in practice, but unlike local eco-industrial parks, such as Kalundborg, the metal networks span the globe. At a global scale it can be seen that the metallurgical and other industrial or waste management processes, form complex networks of processes that are interconnected through mass and energy flows. The networks exhibit typical ecosystem type II properties. First of all, their networked organization enables the relatively high recycling rates of metals. High efficiency and flexibility of metal production, necessary to deal with changing primary/secondary raw materials, are maintained through the partial overlapping functions of the processes and the intensive exchange of by-products and residues. The function of each industrial organism in the networks is partly determined by characteristic features associated with its species (Waelz kiln, ISF etc.), but also partly by its history and development. Similar to nature where each individual of a species exhibits also unique behaviour shaped by its personal experiences and development, each process type has typical strengths and weaknesses but is unique in its behaviour. Figure 1.2 illustrates the combined metallurgical expertise and capacity to deal with impurities and minor elements, in their feed. The inner ring shows the bulk metals, the three outer rings contain the impurities and minor elements, present in the ores the bulk metals are associated with. In order to maximize economic benefits and minimize environmental impact, metal production processes (of metals mostly associated with sulphide ores) have developed knowledge and technological capacity to recover most of these impurities as compounds (the two middle rings), and minimize the elements lost to process residues or emissions (the outer ring of the four rings). A reasonable part of metallurgical expertise and technological capacity of metallurgical processes to deal with changing and complex raw materials is based on operational knowledge, because the physics and thermodynamics of the metallurgical processes are not fully known. Pyrometallurgical processes are complex and typically do not operate at thermodynamic equilibrium conditions, due to multiphase reactions at high temperatures and the resulting strong temperature gradients, complex ill-defined feeds, and large thermal and mass inertia. The dynamics of such processes are difficult to capture in mathematical models. The knowledge base and technological capacity of each process to deal with impurities and minor elements develop over time with variations and gradual changes in the input of each process ("learning-by-doing"). The type of process knowledge is important to deal with the dynamics in feed composition and enable flexible routing through the integrated metal production circuits, but also as a source of metallurgical expertise for the development of new processes, or adapt existing processes to new specifications, feeds or legislation. An example of the latter is the imperial Smelting process for zinc and lead production that over time "learned" to process an increasing amount of secondary materials of widely varying compositions [134, 135, 136] (Figure 3.11). Today the Imperial Smelting process accepts nearly 100% secondary materials. The network resilience/flexibility and development of tacit knowledge point to another parallel with natural ecosystems: conserving biodiversity is critical to survival and development of natural ecosystems. Maintaining a sufficient industrial diversity of metal processes is also critical to conserve the pool of metallurgical expertise as well as technological capacity for production and recycling of metals indicated in the metal wheel.

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[1] Reasons for the development of such diverse and interdependent system include the long life spans of metallurgical processes and the slow development of new technology and alternative process options.

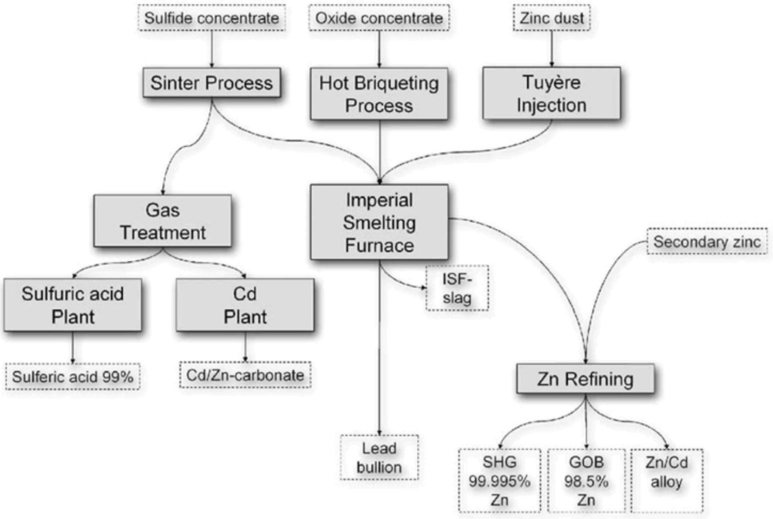

Figure 3.11: Imperial Smelting Process at MIM Hüttenwerke Duisburg GmbH in Duisburg-Wanheim, Germany [134]

3.3 Industrial ecology models for metal production and recycling

The industrial metal resource cycle operates and interacts at different distinct scales: from the exchange of intermediates at process or reactor level, to the global interactions between product manufacture, consumption, solid waste management, mining, and metal production. All of which affect directly and indirectly the flows of metals. This can lead to changes in the production efficiency or environmental impact of one or more metals because of differences in metal recovery efficiencies and environmental performances of each route. In addition, due to local differences between processes, changes in the geographical metal production routes affect the metal metabolism. As mentioned in Chapter 2, the ideas on "industrial metabolism" of Robert Ayres provided means to support the decision-making on industrial ecological principles to key decision-makers, such as regulators, industrial managers or engineers [75, 76]. Ayres suggested to describe the metabolism of the industrial system through detailed "material balances", which could be compiled at different spatial scales, e.g. for a production unit, such as a factory, or the global metal production system. This approach would be suitable to model the metal ecology , which operates and interacts at different distinct scales: from the local exchange of intermediates to the global interactions between resource cycle stages. Without sufficient detail of the underlying networks of processes, the flows between the different stages, and from and into the environment can not be adequately estimated. Inventories in industrial ecology literature often simplify process routes for metals into simple averaging black boxes that represent whole processes, production routes, or even the total production of a metal. In this section, it will be shown that such a level of simplification hardly makes it possible to capture the detail of complex interconnected material processing systems, such as the metals processing system. Consequently, the contribution of these inventories as tools to invoke improvement for metals processing and recycling systems may be questionable. At least two reasons for simplification of process routes have been used. Some may argue that the system is too complicated to completely modelled, or that sufficient data is not (readily) available. The subsequent sections will show that these arguments do not necessarily block the consideration of metal production system at sufficient detail in industrial ecology studies.

3.3.1 Methodology

The metal resource cycles are rather complex and interconnected, which calls for a suitable architecture before they can be simulated satisfactorily [23]. Methodology to construct material balances at the level of a production unit, such as a factory, is well developed (see Chapter 2). As discussed in Chapter 2, Material Flow Analysis (MFA) provides a general architecture or framework to model the throughput of global industrial systems at larger system scales. In these systems different subsystems are generally distinguished involving the extraction, chemical transformation, manufacturing, consumption, recycling and disposal of materials [108]. The methods within the MFA framework typically focus on specific part of the global industrial system, and differ in the way they consider the dynamics of the system. Life cycle analysis (LCA) for example typically lacks a time dimension, whereas Substance Flow Analysis (SFA) typically involves a time dimension. The development of a paradigm embracing the identification and tracing physical flows of materials and energy has been slow, and still lacks a clearly defined methodology [107]. The LCA methodology is a good example of the industrial ecology architecture with regards to the required simplification, i.e. the study breadth and depth. LCA accounts for most industrial ecology studies and contributions to journals and conferences. The development of LCA methodology started in the 1970s, and a standardized LCA framework has been more or less established. Moreover, there is an increasing effort to develop such a methodology and/or combine elements of different methods for wider applicability (e.g. Tukker et al. [114], Van der Voet and Van Oers [116], Daniels and Moore [106]). Because of its advanced state of development LCA can serve as a basis for the further development of these methods. An example of this convergence is the use the LCA framework for SFA [119, 117]. LCA methodology consists of four stages: goal, inventory, impact assessment and interpretation (e.g. ISO [137] and SETAC standards). Despite the long history of standardization of LCA, the methodology is still "under construction". The inventory phase has developed furthest, while interpretation and impact assessment are least advanced. The main focus will be on the inventory phase; goal and impact assessment will only be briefly discussed (in Sections 3.3.2 and 3.5 respectively). Although the ISO standards for LCA provide a starting point for constructing an LCA or SFA, they do not regulate all methodological choices. Consequently, virtually any result can be produced [138]. This holds particularly true for complex systems, such as the global metal production system, even when one considers only parts of it.

3.3.2 Goal, scope and resolution

According to Ekvall and Finnveden [138], the "value of an LCA depends on the extent to which it increases our ability to anticipate environmental consequences of manipulating technological systems". Thus, the goal of any LCA should be to "provide as clear and comprehensive as possible a picture of the environmental consequences of our actions." Obviously, the required "comprehensiveness" of LCA is goal dependent. According to the LCA methodology, establishing the goal of the study includes establishing the boundaries of the picture painted. The procedure for determining the assessment boundaries is iterative and can only be carried out while the inventory analysis is performed [139, 140]. According to the ISO 14041 system boundaries should be selected so that at least all the inputs and outputs are elementary flows[2]. The assessment boundaries are further determined by cut-off criteria, which in turn depend on the level of detail specified in the goal and may be stated in a percentage. If the change in substance or energy due to certain activities falls below a specified level of change, the process chain leading to the creation of the substance or energy needs not to be included in the study [141, 137, 138]. Todd and Curran [142] argue that industrial processes are so extensively interconnected globally that complete consideration of all these interdependencies is prohibitive. The definition of the scope should be such that the breadth and depth of the study are compatible with the stated goal. Thus based on the stated goal, decisions must be made on which processes or activities will be included, and to which extent these activities or processes belong to the foreground or background systems. Todd and Curran [142] discuss a variety of possible approaches for simplifying the LCI methodology and reducing the amount of data required. Typically, approaches to streamlining have entailed simplification of the life-cycle inventory (LCI) through the elimination of life-cycle stages (e.g., cradle-to-gate studies that ignore activities after the production stage) or reducing the data required on the unit process networks (e.g., by applying thresholds or cut-off criteria or by limiting the analysis to first tier contributions). In this context, Azapagic and Clift [143, 144] found it useful to distinguish between a "foreground" and a "background" system. The foreground system is the set of processes that are directly affected by the goal of the study, while the background system is the set of processes that supply the foreground system with energy and materials.

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[2] Elementary flows refer to (i) material or energy flows entering the system being studied, which has been drawn from the environment without previous human transformation, and (ii) material or energy flows leaving the system being studied, which is discarded into the environment without subsequent human transformation.

If the change in the background system is relatively small the system can be regarded as unaffected. If changes in the foreground system cause larger changes in the background system, the affected parts of the background system must be included in the foreground system. Some background systems, such as those that produce energy or transport metal products, do not show complex interdependencies, and effect of foreground changes on these systems can easily be predicted. Other systems are so complex that it is difficult to predict to what extent a change of a subsystem affects other subsystems, and thus what boundaries are needed or what level of detail is required.

3.3.3 Interdependence between metal production circuits

Metals are typically produced via globally interconnected production circuits. Figure 3.12 shows a generalized representation of the interconnections in the production of eleven metals. The dotted squares in the middle represent the major intermediates connecting the different metal production circuits. The figure shows how the production or recovery of a single metal is related to the generation or recovery of other metals. Figure 3.12 shows that production of a number of metals from the interconnected metal infrastructure is complex, as most of these must be circulated between two or more production circuits before they are concentrated enough to make their extraction possible, and their recovery as a metal profitable. For instance, silver and bismuth in ores are concentrated in Kroll Betterton crust, Parkes crust and anode slimes in the lead(-zinc) circuit, before they can be recovered in the silver or bismuth circuits. PGM are circulated between even more circuits. A model based on a black box approach for each of the metal production circuits can not sufficiently capture the interdependence in metal production and recycling. The interdependence between the metal production circuits is a consequence of the interconnections of the metal processes that constitute the metal production circuits in Figure 3.12. Without sufficient detail on the underlying networks of processes, the flows between the different circuits, but also from and into the environment can not be adequately estimated. Without considering the exchanges of intermediates between metal production circuits, and the interconnections between production and recycling of the different metals process level, one can not predict to what extent a change of a subsystem affects other subsystems, and thus what boundaries are needed or what level of detail is required. In other words, because the metal production and recycling capacity is realized by a dynamic network of reactors, tools to invoke improvement in this capacity also require modelling at level of reactors.

3.3.4 Interdependence in metal production processes

Figure 3.13 shows a generalized metal production circuit consisting of three basic metal production routes:

- oxidative smelting route,
- reductive smelting route, and
- hydrometallurgical route.

These routes are all capable of separating a large number of elements at the same time, but with various degrees of efficiency. The ores are mined in either open pit or underground, subsequently concentrated through crushing, grinding and flotation to reduce the volume to be transported. A single ore can produce several concentrates: the processing of "zinc ore"

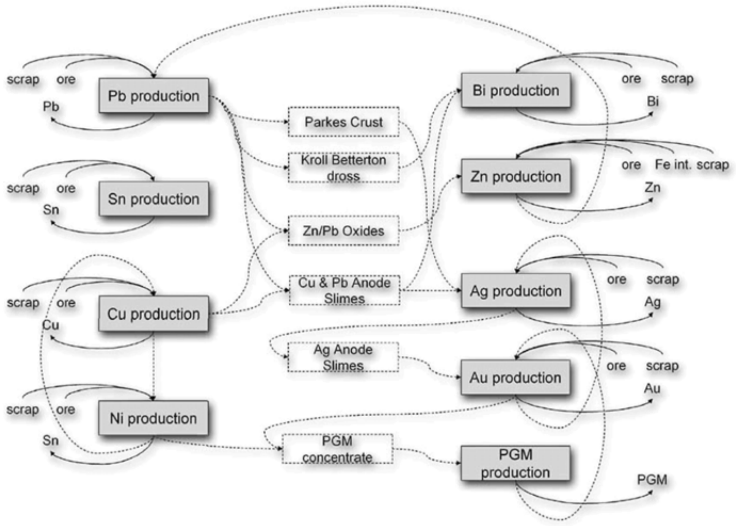

Figure 3.12: Overview of the interconnected production system of eleven metals *(dotted squares represent important intermediates connecting the metal production circuits)*

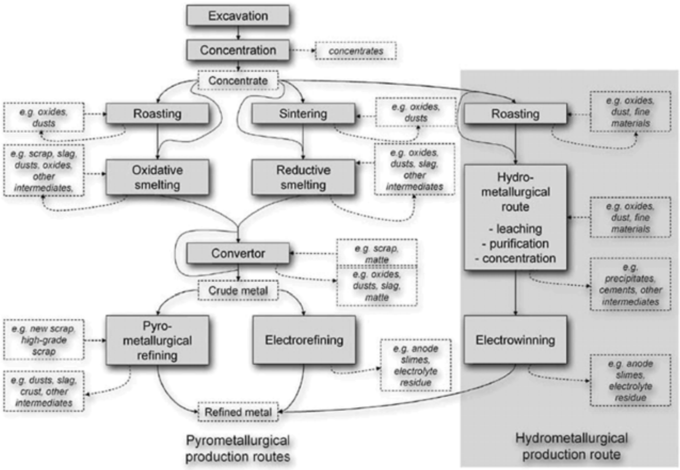

Figure 3.13: Generalized flowchart of the extraction and production of a metal *(dotted squares give examples of possible intermediates connecting the different metal production routes)*

generates zinc, lead and copper concentrates. Both of the (primary) pyrometallurgical metal production routes, oxidative and reductive smelting, start with the smelting of the ore to a crude metal and removing the gangue material and the main impurities. Subsequently, the crude metal is refined to a pure metal. In reductive smelting, usually sulphide ores are smelted under a reducing atmosphere together with a flux. The valuable metals are collected as metal sulphides in the "matte phase", while the gangue material is collected as oxides in the slag. A density difference will ensure that these two phases segregate. The matte phase can be further treated in a converter to remove remaining impurities, mostly iron, and to convert the matte phase into the crude metal. In oxidative smelting concentrates are smelted under an oxidizing atmosphere. The resulting metal oxides are subsequently reduced with carbon to produce metals. The gangue material will not react and remain in oxide form. The density difference between the phases will ensure that the metal phase separates from the oxide slag. The metal phase can be further processed in a convertor prior to the refining step. Some metals are produced from sulphide ores and need to be calcined (or "roasted") to oxides before the can be treated through oxidative smelting. The crude metal produced via either route is refined using pyrometallurgical methods, or electrowinning. In pyrometallurgical refining impurities are removed in several steps. In electrorefining, anodes of the crude metal and "clean" cathodes are put in an electrolyte bath. By running a current from the anode to the cathode, the metal will dissolve and selectively deposit on the cathode. Impurities in the anode either are dissolved in the electrolyte, or collected as anode slimes. Some metal concentrates, such as copper or zinc, can be processed directly into refined metals through hydrometallurgical routes. In the hydrometallurgical process metals are produced electrolytically. First, the concentrates are typically oxidized in a fluid bed roaster. This roasting (or calcination) step is followed by leaching to bring the metal oxides into solution. After purification and concentration, the metal-bearing solution is electrolyzed to produce the metal. Dependent on the processing route, a large number of elements are separated together with the "carrier" metal with various degrees of efficiency. In turn, the composition of the available raw materials determines which route the materials can follow from concentrate (or scrap) to refined metal (see Section 3.2.2). At each process step in the different production routes, metals and other materials are separated; the resulting residues, intermediates or concentrates can be used in other production routes. At the same time, primary and secondary concentrates, intermediates and residues of other production and recovery routes are consumed and further refined. The raw materials used in each route, the geographic location, the related sophistication of the process steps employed, and differences in environmental legislation determine the actual composition and quantity of the intermediates produced, consumed and disposed of. Consequently, the modelling "unity" should be a process step, rather than a process plant. This approach would link up with the modelling and data acquisition methods in chemical engineering, which are also based on mass balances over individual (but connected) process steps, and thus ensures the availability of reliable data on process performance.

3.3.5 Goal and scope revisited

Although complete consideration of all the interdependencies between industrial processes is laborious, it still may be necessary for adequate modelling of metal production and recycling. Due to the complexity and non-linearity of the metal production system, it is difficult to estimate in advance the level of detail required. A change in the production volume of a metal, or the set of processes employed in its production, may have large consequences for the production of other metals. In addition, a lack of system understanding and/or data may lead to arbitrary cut-off limits, which introduces bias and can lead to errors in estimates of environmental impact. According to Todd and Curran [142], it may thus be necessary to supplement the LCA with other tools or methods to provide a sound basis for decision-making. The metal wheel (Figure 1.2) can provide for a valuable tool to establish the different interdependencies between the production routes of different metals [16]. Estimating the effect of a change in the production of one metal on other metals, however, would call for comprehensive modelling of the interconnected metal production system. SFA-type models can provide for "unifying cores" as Dutchin and Hertwich [105] suggested, or provide a basis for the quantitative systemic models that Allenby [14] called for to support policy and other industrial ecology activities that span across multiple system levels. Such a model is presented in Chapter 5 and further described in Appendix B.

3.4 Data availability

Different industrial ecology models can be distinguished, which differ particularly in the way they consider dynamics of the systems: the changes in flow and accumulations. As a consequence, data requirements vary considerably per model. The different types of models are briefly discussed below.

3.4.1 Mass balance models

Metal production system can be seen as a dynamic network of interdependent process steps (network nodes) that are interconnected through the exchange of intermediates (network arcs). The dynamics in metal processing can be captured by modelling the systems as a network of nodes. In the nodes (process steps) materials are transformed into products and intermediates. Between these nodes materials (intermediates) flow and accumulate. The flows and accumulation are a function of the raw materials entering, and the products flowing out the network. De Haes and Van der Voet [41] distinguish at least three types of SFA models for the modelling of transformations, flows and accumulations or stocks in the industrial system. These mass balance models differ in resolution and in the way they consider dynamics: (i) bookkeeping, (ii) stationary modelling and (iii) dynamic modelling. In the bookkeeping model, a flowchart for the system with all the stocks, flows and processes is made. For a given period, empirical data on the flows and stocks are collected. This method allows policy makers to spot trends and evaluate effects of certain changes. Secondly, a stationary model can be used, in which the processes are formalized in such a way that the outputs can be formally computed from the inputs, or vice versa, the inputs can be computed so as to satisfy a given set of output values. Apart from possible changes in the immobile stocks and from changes outside the given system, it describes a stationary situation. In principle, data from the bookkeeping overview can be used to calibrate the mathematical equations of the processes. It is to be preferred to use data regarding the distribution characteristics of the processes themselves, if available, in order to avoid the inclusion of coincidental factors in the equations. The core of the stationary model is thus the development of a consistent mathematical structure, which renders it possible to specify relations between the different flows and stocks within the system. In this way, specific problem flows can be analysed with regard to their origins. Also, the effectiveness of certain developments or measures can be estimated by comparative static analysis, which is not possible with the bookkeeping approach. Where stationary modelling pictures one (or more) distinct system steady states, dynamic modelling allows analyzing the path towards the static equilibrium. Thus, it is the most suitable method for scenario analysis, and system or product design under dynamic conditions. As can be seen from the dynamics and interdependence in metal production, this is also the preferred method for modelling the interconnected industrial metal resource cycles. However, dynamic modelling also has the largest data requirements. When (accurate) data is lacking, dynamic modelling is not automatically preferred over the more, robust stationary approach. If the additional data can be obtained, software packages, such as Mathworks's Simulink (Matlab), allow for an easy conversion of the stationary model into a dynamic model as will be illustrated in Chapter 5.

3.4.2 Data requirements and availability

The choice for a certain model type or level of detail (breadth and depth) is constrained by the availability of adequate data, and the capability of shaping this data into an internally consistent model of the system. Data available for modelling of the metal cycles is highly variable in quality, and level of detail. To construct mass balances for a process step, data on process inflows and outflows must be obtained. The data is sometimes hardly available, and must be obtained from very heterogeneous sources (e.g. encyclopaedia, reference books, conference proceedings and literature reports, industry and internet). A complication in collecting representative information on process steps is that their performance differs due to developed tacit knowledge or applicable environmental standards for example. Preferably, therefore, different sets of input and output data must be found for each process type in the mass balances representing their distribution around the globe. This allows reliable estimates of the average global performance per process step. In addition to obtaining data from credible sources, another constraint is the consistency of the data [145]. The consistency must always be verified using mass balance conditions. Another constraint is the ability to capture the behaviour of system components in mass-balances. The operational knowledge in the processes controlling the behaviour is tacit knowledge : it can not easily be captured in first principle models or be transferred, but is based on experience and gut feeling gathered over the years. Even in process control, it is accepted that a considerable percentage of the control is based on the experience of human "sensors", and is specific for the process. It is part of the collective knowledge (or "brain") of the process. Consequently, the effect of change on process operation is difficult to model in mass balances. Thus, to support the decision-making through detailed "material balances", these mass balances must be regularly updated to reflect changes in the materials transformations in processes. In order to describe the metabolism of the metal production system through detailed mass balances, three types of data are required. First, the description requires the elementary or chemical compositions of process inputs and outputs to construct mass balances of the individual processes (material transformations). Second, metallurgical system understanding and overview is necessary to combine the process mass balances into the interconnected metal production circuits (network structure). Finally, general metal statistics are needed to calibrate mining and metal production flowcharts, e.g. global mining, metal production and recycling/disposal (raw materials entering and products flowing out the network).

Metal production and recycling

For a number of metals, the metallurgical industry already collects and publishes detailed inventories of the different processes employed, which can be used for quantitative modelling. Nevertheless, data coverage was not sufficient to obtain representative inventories for each process in the metal extraction and production system. The next section shows that mass balance conditions can be used to check data consistency, largely fill in the missing data, reduce errors, and construct an internally consistent map of the mining and metal production stages. A detailed description of the interdependent process steps involved in the production of these metals is provided in Appendix B.

Solid Waste Management

Secondary materials that substitute the primary ore concentrates may have very different compositions. As a consequence, the recycling of these raw materials may have a considerable effect on the metals that are separated together with the "carrier" metal. This feedback of secondary resources into the industrial processes is a major challenge for modelling the metal metabolism through detailed mass balances. A distinction can be made between production and end-of-life (EOL) waste. In the production of metals residues are generated (e.g. slag or flue dust) for which no recovery route exists, or intermediates for which there is no demand or recovery capacity. The composition of these wastes follows from the mass balances of the metal production processes. Data on the waste arising from the manufacture of final products or the discarding of these products after use, and on the subsequent separation processes into suitable raw materials for metal production is not sufficient to model the global metal metabolism through detailed mass balances.

Manufacture and Consumption

The manufacture and consumption stages in the metal resource cycles determine when and how secondary metal resources become available for recycling, or are lost through dissipative use (Figure 3.14). Graedel et al. [110] observed that following the production of metals via semi-finished products to the final products, the metal flows not only become highly complex but the statistics become very sparse. Nickel, for example, is used in over 300 000 products including consumer, industrial, military, transport/aerospace, marine and architectural applications [146].

Distributed properties

Data availability is not sufficient to allow a bottom-up construction of the many product manufacturing routes based on mass balances of individual manufacturing processes involved. As a consequence, product compositions, emissions and energy consumption of the manufacturing stage can not adequately be estimated through bottom-up approaches. For similar reasons, the residence times, energy consumption or the dissipation into the environment during use can not adequately be estimated through a bottom-up approach either. The residence time of metals in the consumption phase, for example, is an aggregate of the lifespans of the many different products the metals are used in. The actual lifespan of each of these products depends on individual consumer preferences and decisions to discard the products[3], shows considerable variation per product and may also change considerably over time. In the modelling of waste flows from consumption stocks, Kleijn et. al. [147] suggest to model the stock as a "time buffer". Metals in use (economic stocks) and waste generation can then be approximated using general metal statistics that report on the different end uses of metals as function of time, and estimates of life span distributions for these end uses or rather end use categories (A1 in Figure 3.14). The total economic stocks of metals can than be determined by integration over the longest life span. The actual composition of the old scrap from separation processes can be estimated (A2 in Figure 3.14) similarly by partitioning the end use categories to standardized routes for typical waste categories (Municipal Solid Waste, Wasted Electric and Electronic Equipment or End-of-Life Vehicles etc.). Further detail on data availability of

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[3] Reasons for discarding include technical reasons, e.g. the product is irreparable, economic reasons, e.g. the cost of repairing the product is uneconomic, functional, e.g. new products have improved features and/or psychological reasons, e.g. the desire for new and fashionable products.

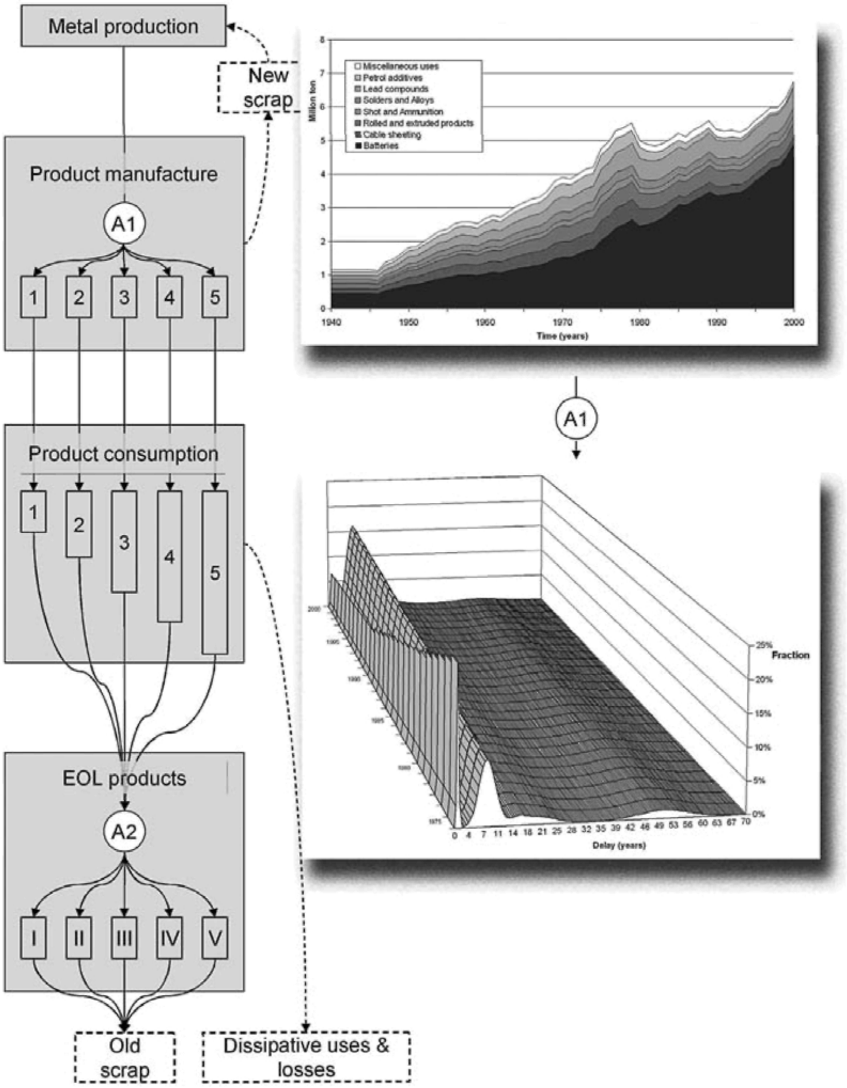

Figure 3.14: Estimation of metals in stock and waste generation using metal statistics on the different end uses of metals

the manufacture, consumption and solid waste management stages and this approach can be found in the appendices.

3.4.3 Data reconciliation

Because the processes were reported for different reasons, and with different levels of detail and completeness, mass balances for individual processes often could not be closed. Madron [148] and later Veverka and Madron [149] gave overviews of data reconciliation: a set of methods used to adjust the experimental data to reduce and possibly eliminate discrepancies in the mass balance. Data reconciliation is basically minimizing a sum of errors (the difference between each measured data and its reconciled value) weighted by the measurement error, subject to a number of constraints (the mass balance equations). The mathematical denotation for the data reconciliation is given by Eqs. 3.1 to 3.5.

$$J(Y) = \sum_p \sum_i J_{pi}(Y) \tag{3.1}$$

$$J_i(Y) = \left[\frac{Q_{pi} - \overline{Q}_{pi}}{\sigma_{pi} \times Q_{pi}}\right] + \sum \left[\frac{P_{pik} - \overline{P}_{pik}}{\sigma_{pik} \times P_{pik}}\right]^2 \tag{3.2}$$

In which:

Q_{pi}, P_{pik}	Reconciled magnitudes
$\sigma_{pi}, \sigma_{pik}$	measurement error
$\overline{Q}_{pi}, \overline{P}_{pik}$	measured magnitudes
$\overline{Q}_{pi}; Q_{pi}$	flow rate of phase p in stream i
$\overline{P}_{pik}; P_{pik}$	fraction of component k of phase p in stream i

Adjustments to experimental data are subjected to a number of restrictions, viz. the conservation of global flow rate (Eq. 3.3), the conservation of global and elements flow rates (Eq. 3.4) and the data integrity constraint (Eq. 3.5).

$$\sum_k P_{pik} = 1 \tag{3.3}$$

$$\sum_i m_{ij} \cdot Q_{pi} \cdot P_{pik} = 0 \tag{3.4}$$

$$\sum_i m_{ij} \cdot Q_{pi} = 0 \tag{3.5}$$

In the reconciliation of the mass balances of processes for the dynamic modelling, the data is not based on measurements, but on processing data of plants around the world found in the literature. The essentials of the data reconciliation technique, however, remain the same. Calculation of the average compositions as a basis for constructing the mass balance normally does not result in a completed mass balance of the unit operation employing linear algebra. Using the standard deviation in the data as a measure for the accuracy of the data, a closed mass balance can be obtained using data reconciliation. Because the thermodynamics and physics of the processes are not always fully understood, and process outputs are partially controlled with the tacit knowledge of the process crew, these split-factors are difficult to determine and can vary between different processes, or with feed composition. The work of

Reuter [23] showed that the approach taken provides for a good representation for average process operation. Application of data reconciliation methods significantly reduces gaps and inconsistencies in the mass balances of the individual process, and produces reliable estimates of feed, (by)product and residue flows. The software used for data reconciliation is Excel 2000. The maximum number of elements that can be reconciled is limited by the computational capacity of Excel's standard solver, and therefore only critical elements were included in the mass balance. In Appendix B and Appendix C.1, the modelling in Simulink and the process of data reconciliation is explained. Further details and the raw data can be found in Scholte [150] and van Tweel [151].

In combination with statistics on the abundance of processes, production of metals and ore extraction, these reconciled balances can be used to obtain the process inputs or outputs of other processes (and thus close their mass balances), or reduce inconsistency in the interconnections in the production routes. For instance, the elemental compositions of ores found in literature often are limited to their major (or valuable) components. The input and output data of the crude metal production often provided higher detail. Data on the composition of concentrates or the production of co-elements and intermediates from the different reconciled processes downstream were used to derive more complete ore compositions. Data reconciliation is thus a powerful tool to improve data quality and check the internal consistency, but requires considerable effort. Figure 3.15 shows the reconciled mass flows in the interconnected metal production system. A detailed overview of the mass balances of different processes can be found in the Appendix B. Data reconciliation can only be used when mass balance conditions can be imposed. It is for example difficult to apply to end-of-pipe or auxiliary equipment of processes, such as off-gas treatment. Because off-gas treatment equipment varies widely around the globe [97, 152, 153], sulphur recovery efficiency per process or production circuit can not be estimated from the sulphur production statistics, but recovery efficiencies for off gas treatment units can be obtained from literature. The efficiencies for sulphur, carbon monoxide and dioxide, nitrous oxides and flue dust capture in the production of one metal can be used to estimate the efficiencies of an other metal for which more data is available (e.g. copper) with some basic chemical assumptions. When mass balance conditions can not be used to reduce uncertainty, the effect of the uncertainty in these estimates on the model outcomes should be tested by sensitivity analysis (see Appendix B).

3.5 Potential for industrial ecology: Convergence of methods

Advancing sustainability through a deliberate and rational eco-design of the industrial activities could benefit greatly from properly constructed quantitative models that can support and connect the different prescriptive efforts, and thus assist in their co-ordination. As argued in the introduction and Chapter 2, the systemic perspective of industrial ecology calls for a shift from dealing with isolated, relatively simple systems to managing complex, interdependent systems such as the metal production and recycling system. To visualize the behaviour of such a system and link the behaviour to environmental issues, quantitative modelling involves two stages: first, the goal and inventory stage to predict flows and transformations across system levels, as well as the emissions in and extractions from the environment caused by flows and transformations; second the impact assessment stage, which translates these emissions and extractions into impacts to the environment, which are understandable to decision-makers. As a consequence of the interdependence in metal production and recycling, the metallurgical system is difficult to adequately capture in quantitative models. Modelling metal production

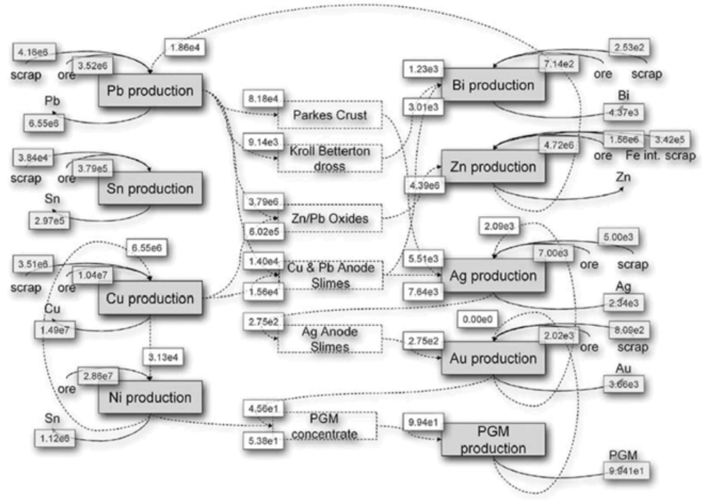

Figure 3.15: Simplified representation of the mass flows in the interconnected production system of eleven metals

and recycling is possible with present industrial ecology (MFA) methods, but is very laborious: it requires an inventory of reconciled mass balances of all process steps from ore or waste to refined metal. The amount of work involved can be an impediment for some studies to consider the interdependence in metals production. These studies should then be supported by other models, such as SFA models at the right resolution. This illustrates the importance of a consistent methodological framework spanning all MFA models. Convergence is not only essential for goal and inventory stage, but also for the impact assessment phase. Currently many competing mechanisms are available for impact assessment. Each of these historically developed to support the decision-making process in different ways, and consequently lead to different outcomes and have different data requirements. This could result in problems with using the results, or underlying analyses and data of one study in another.

Cadre 3.1
Impact assessment method

There are basically three ways of impact assessment: based on "begin-points", "mid-points" and "end-points". Begin-point assessment uses the inventory data with little or no further specification or aggregation. In most SFA studies, for example, the output is defined in terms of flows and accumulations of the material under study, or through the use of aggregation indicators like recycling rate and efficiency. These indicators are used in reference to a norm or ideal value; deviation from this reference value can indicate problems. The relevance of the analysis is generally directly related to the hazardous character of the chosen material and will need no further specification [117]. In some cases, there is an explicit need for further elaboration of the SFA results, for example, if a group of substances is studied. In such a case, it is difficult to make a comprehensive interpretation of the emission inventory data without some form of aggregation. The impact assessment of SFA based on mid-points and end-points is far less developed [41]. For LCA studies there is a wide range of competing methods that link the life cycle inventories to environmental impact [154, 109]. Each of these methods could be used for assessment, though the outcome can differ for each method [155]. The methods can be classified in two groups of approaches: the end-point (or environmental damage) approach and mid-point (or environmental themes) approach [156, 120]. Simply put, the mid-point category indicators can be defined as an attempt to model the intervention-impact-damage chain to a point where knowledge is still fairly sure and complete, and where the remaining end of this chain is only conceptually or partially known. End-point category indicators can be regarded as an attempt to let decision-makers decide on what they can understand, and to use scientific knowledge, even if unsure and incomplete, to specify the category indicators at this comprehensible level [120]. An example of this is the climate change impact on human health. The central difference between the mid-point and end-point approaches thus lies in how the valuation[4] *step is integrated in the analysis: the mid-point approach separates characterization and valuation. Those partaking in the valuation exercise determine the relative importance of the indicators for each theme (valuation). In the end-point method, the relative importance is expressed in the calculated damage indicator. As a consequence, the damage approach allows a direct comparison of the damage resulting from different impact categories, which eases decision-making. In addition, the damages are closer to our concerns. However, the prediction of damage (end-points) resulting from a change in the stressors is difficult due to the complexity of the underlying environmental, physiological, and economic processes [156]. Thus*

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[4] The valuation step specifies and aggregates the inventory outcomes in terms of their perceived contribution to public health and environmental impact.

although the end-points methods provides for the clearest link to the environmental problems, and allows for easy interpretation through reduction of the number of variables, care must be taken when interpreting these results. Because of the advantages and disadvantages of both methods, it is not surprising that there is increased consensus about the desirability to combine midpoints and endpoint indicators in a uniform framework. Recently a project started to develop a framework in which midpoints and endpoints support each based on CML (mid-point) and EcoIndicator '99 (end-point) methods [118, 120]. A possible way to interpret the outcome of SFA studies is specifying the contributions of the substances to a number of environmental issues or environmental impact categories, such as global warming, ozone depletion, and acidification. This approach links up with the development of LCA impact assessment methodology. An example of such an approach is the recent SFA study on chlorinated hydrocarbons in The Netherlands [115, 117] that used environmental impact categories such as global warming, ozone depletion and ecotoxicity. Other examples include the studies on chlorine and PVC for the Dutch government and Norsk Hydro that also combined elements of SFA and Life Cycle Impact Assessment (LCIA) [115, 112, 113]. Based on their studies, Tukker and Klein [114] conclude that environmental evaluation methods like SFA and LCA can successfully be used in combination. A problem of using LCA approaches in SFA (or for the comparison with SFA study outcomes) is that LCA does not consider time dependency: the effects of the damage over time, e.g. the actual resource depletion, are not accounted for in the related impact assessment methods. For instance, if metals ores are mined over time, the available stocks decrease and the seriousness of further depletion increases. This should be realized when interpreting the impact assessment results. A dynamic SFA simulates the effect of future developments on the system and its environment. Rather than indicating damage scores due to resource depletion, it simulates the decrease of the available resource stock in a given scenario. Therefore, the stocks and flows as a function of time of simulations are available for detailed analysis.

From the brief discussion of different impact assessment methods in LCA and SFA it showed the many different impacts assessment mechanisms. In principle all of these can be used, though they produce different results. For consistency between different study outcomes, it is stated in the ISO (14042) standard that impact assessment results can not be the only source of information for comparative assertions. Impact assessment is basically viewed as a way to interpret the inventory in the context of the study goal. In this view the inventory determines the subsequent impact assessment. However, the opposite is also true: the requirements of the decisions or actions for which the study is undertaken dictate the type of impact assessment to be included. As the different methods have different data requirements, the data requirements for the impact assessment are, then, the major drivers for the inventory [157]. This bilateral interdependence shows that industrial ecologists must clearly define their data requirements by further developing the inventory and impact assessment methodology. Only if a model methodology is well defined, data can be collected and published in a structured way, and study outcomes can be compared and effectively used in (and interchanged with) different studies. This chapter has focused mainly on the inventory stage. Although the ISO standards for LCA provide a starting point for constructing an LCA or SFA, they do not regulate all methodological choices, and as a consequence virtually any result can be produced [138]. The metal wheel is introduced as a simple means to visualize interdependencies in metal production and recycling, and can be used in the establishment of system boundaries for environmental impact studies. Based on the wheel, a methodological basis or suitable inventory architecture has been presented as a basis for tools to invoke improvement for metal processing and recycling systems.

3.6 Summary

In comparison with the well-known examples of eco-industrial parks, the interconnected metal production and recycling system is a less recognized example of industrial ecology in practice. The metallurgical industries minimized the use of resources and production of wastes by interchanging resources, intermediates and residues between processes. As a result, the production of metals is so interdependent that they can hardly be considered separately. The metal production and recycling system is an excellent case to study the potential of the current descriptive approaches to design and manage industrial systems as industrial ecosystems. To date, however, industrial ecology studies on metals production and recycling lack a sufficient depth to invoke improvement for metal processing and recycling systems. Because the metal production and recycling capacity is realized by a dynamic network of reactors, tools to invoke improvement in this capacity also require modelling at level of reactors. The metal wheel is introduced as a simple means to visualize the interdependencies in metals processing. It can be used in the establishment of system boundaries. The (dynamic) interdependence in metals processing resulting from the ecosystem organization calls for a different model approach than for other resources that are less interdependent. Capturing the interdependence in MFA models requires modelling the interconnections between the metal process steps, i.e. based on detailed mass balances of individual processes and process steps. Without sufficient detail on the underlying networks of process steps, the flows between the different metal production circuits, but also from and into the environment can not be adequately estimated. To construct a quantitative description of the metal cycles, it is necessary to rely on a mix of information from a great many sources often collected for different purposes, with different detail and accuracy. Statistical methods, in particular data reconciliation, are necessary to ensure the reliability and consistency of the data at the different system levels. The required efforts to do so may be an impediment for many (LCA) studies on the metals production and recycling system or parts of it. Additional tools to complement these (LCA) studies are required to calculate changes in the metallurgy. For these tools SFA models can be used based on reconciled mass balances of all metallurgical process steps involved. Because this is a very data-intensive process, industrial ecologists must clearly define their data requirements. Only if a model methodology is well defined, data can be collected and published in a structured way. In this context, methodological convergence in the current trends in research and modelling of environment related flows in the physical economy is essential. Such convergence could yield significant benefits with respect to the underlying data collection, accessibility and conformity. Thus it could reduce the effort of considering the interdependences in metallurgical systems. For this reason, the data underlying the quantitative description is reported in detail in the appendices. The data can serve as a solid basis for other studies on metals processing and recovery. It is essential that the metallurgical, the manufacturing and waste management industries collect and present data on the different stages in the metal cycles (i) in a way that allows modelling of these systems, and (ii) in literature available to industrial ecologists (or other people that construct material inventories) rather than in specialist or professional literature, conference proceedings etc. alone. Availability of current data is even more important considering that the metallurgical system is an evolving system. The tacit knowledge plays an important role in the development of the performance of existing processes and of the development of new processes, but can hardly be modelled. For representative modelling of metallurgical systems, industry must ensure that model data and flowsheets (the configuration of the processes) represent industrial practice.

Chapter 4

A prescription for the metal cycles

In Chapter 2, the apparent value of an integrated description of the flows and transformations and their impacts on the environment across various levels in the physical economy was discussed for the industrial ecology goal. In Chapter 3, an integrated description of the metal cycles was provided. In this chapter a multidisciplinary, qualitative prescription for the metal cycles is given. Prescriptive studies address the analysis and control of the development and patterns of materials and energy through optimizing the ensemble of considerations that are involved. The metal cycle is therefore investigated from a multidisciplinary, ecological perspective, with a focus on waste processing and metals production (Sections 4.1 - 4.4). It will be shown that a solid and detailed understanding of metal processing and metal use is essential to assess and address the problems of industrial ecology strategies, including the risk of loss of the entire stock of high-quality metals with increasing recovery rates. Descriptive approaches can not always supply all the information necessary for control of the development and patterns of materials and energy, but may serve as a tool to assist communication between the parties involved. Finally, the control strategies for "sustainable" production and recycling of metals are reflected on (Section 4.5).

4.1 Metal ecology

In the previous chapter, the industrial "metabolism" underlying the global metal cycles was investigated as a case study. In Chapter 2 it was illustrated that descriptive approaches provide the quantitative frameworks to show the technological aspects of an economy operate and may assist in their restructuring if desired. This chapter investigates how these approaches can to assist a restructuring. In the handbook on industrial ecology, Allenby [14] predicted that the metal sector is one of the sectors that will undergo significant changes on the road to sustainability. It will be shown that an ecological perspective is essential to assess and address the problems for such significant changes. In an ecological perspective, one looks at relationships between systems components mutually, and between organisms and their environment. The term ecology refers to the relationships between organisms and their environment. The term "metal ecology" will be used to refer to the relationships between metals extraction, production, manufacture and recovery processes (the metal "organisms"), as well as the interaction with non-technical, environmental factors driving the system, such as legislation, and the natural environment (their environment). Metals that participate in linked cycles can not be analyzed independently as many life cycle assessment studies attempt to do. As a consequence, process design, waste management, metals production and legislation/policy can not be considered separately either. They are cross-linked in metal production and recycling, combined in products and connected through feedback loops. The production, use and recycling of each metal thus affects the others. In theory, metals can be recycled infinitely and may be considered renewable resources. Plastics do not have this property since molecule chains are always broken due to thermal processing during recycling, ultra violet light, etc. as a function of time. In the management of metal cycles, therefore, a key objective in accordance with industrial ecology would be to achieve complete recovery of metals from sources in industrial society. Only thus, can the level of the stock of metals available for economic use be maintained and depletion of mineral resources prevented. In practice, however, the dilution of metals-that is, their mixing and contamination- associated with use and recovery of metal is a major problem, because it limits the usability of secondary metals. A solid and detailed understanding of what might be termed, metal ecology, is essential to assess and address this problem: one needs to understand not only the processes and the technology, but also the relationships between processes mutually and between them and their environment. To our knowledge, neither in industrial ecology literature, nor in metallurgy literature studies or models have been reported that considered the dynamic interdependence in the metal ecology outlined in the sections below.

4.2 Goals for "sustainable" metal metabolism

Industrial ecology promotes an industrial evolution that considers the characteristics of the natural world. Prescriptive approaches consider the natural world in at least two ways: First, industrial activities must be reorganized according to the limitations carrying capacity of the natural world upon which industrial activities are founded. Second, the organization of the natural world is used as a model for industrial activities: industrial activities must be restructured according to type III ecosystem principles (see Chapter 2). The different prescriptive approaches use both elements to develop strategies that minimize the environmental burden created by the releases of energy and materials into the environment, and to maximize the efficiency of materials and energy use.

From an industrial ecology point of view, the industrial system is viewed as a physical system in and through which materials and energy flow and change into raw materials, products and residues, and from which wastes and excess materials may "leak" or be disposed of causing damage to the environmental or human health. This is illustrated in Figure 4.1: the transformations in each stage of the resource cycle lead to material and energy leaks or losses. If this perspective is adopted, two complementary strategies follow: (i) strategies aimed at prevention of the emissions from metal production and use by minimizing the circulation of materials, and (ii) strategies aimed at containing materials in the "technosphere". Dematerialization and detoxification are examples of the first strategy. Detoxification involves avoiding and/or minimizing the creation and transport of toxic and hazardous materials such as lead. Dematerialization, closely related to eco-efficiency, aims to provide the same or more service at less environmental impact. The first strategy thus views the use and production of metal as an important source of environmental burden, and prescribes a minimized use of metal to reduce impact. The use of metals can be reduced by the redesign or substitution of products and services. The second strategy recognizes that most metals are difficult to replace, strategies of the first type alone cannot provide "therapy" for all emissions. Assum-

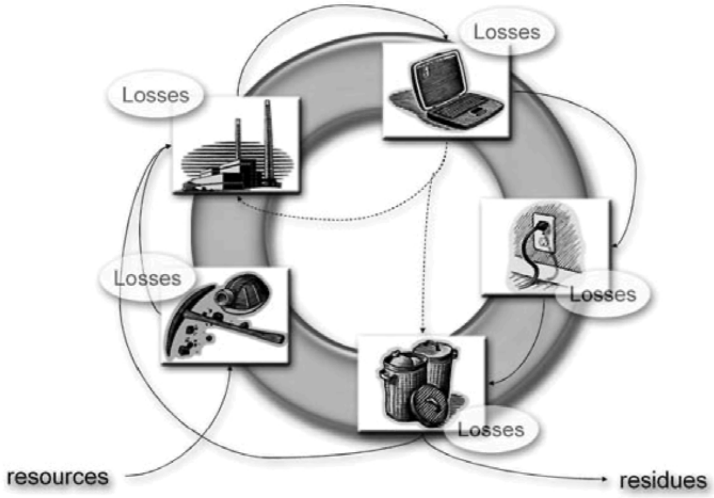

Figure 4.1: Generalized metal resource cycle: metal resources are mined and concentrated (mining), processed in metals (metal production), manufactured, consumed (product manufacture) and finally disposed of or recycled (SWM).

ing continued use of metal, this sets a new challenge to the production, manufacturing and waste processing infrastructure. To contain metal in the resource cycle and reduce leaks and disposal, technologies (and products) must be redesigned and rearranged to reduce the use of materials that disperse beyond possibility of recapture. Waste generation and disposal must be minimized, and all remaining waste must be defined as potential products for which markets must be sought. Containment of metal is also important from a resource management perspective. Only by a (near) complete recovery of metals from sources in industrial society, the level of stock of metals available for economic use can be maintained and depletion of mineral resources prevented[1]

4.3 Dynamics in the resource cycles

The basis of prescriptive approaches lies in the analysis of the role of the metal organisms, their current organization and their surroundings in the implementation of the strategies outlined above. Many industrial ecologists, including Verhoef et al. [7], Andersson and Råde [158], Sagar and Frosch [101], Oldenburg and Geiser [102], Reuter [23, 33], Weston and Ruth [125] and Ruth [159], recognized the need to study the dynamics of industrial ecosystems. Because of the interconnectedness of process design, waste management and metal production, and of metallurgical processes mutually, this holds especially true for the

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[1] Current estimates of world population bringing the world population above 10 billion people in 2050, and the economic growth in developing countries necessary to bring the per capita GNP at least at the level of the developed country today, would drastically increase our need for resources. Prudent use of non-renewable resources is therefore essential to fulfil the needs of future generations, but also to minimize impacts on the environment today.

metal ecology. The production of most metals is still increasing, which (ceteris paribus) will result in higher metal emissions (to water, air and soil), and/or in metal accumulation in the economy, i.e. in capital goods, intermediate products, consumer goods and wastes. If strategies to reduce emissions from metals production and use overlook the accumulation, emissions may be only temporarily decreasing and may well increase in the future -e.g. through corrosion, inadequately controlled incineration and landfill or metal dilution (cf. Ayres et al. [160], Stigliani and Anderberg [161], Bergbäck and Lohm [162], Verhoef et al. [7]). Too strict environmental measures may also export the metals and production/recycling facilities to foreign countries and thus shift the problem abroad. The restructuring of the metal sector is thus a dynamic problem, which is dependent on the dynamics of all components constituting the metal ecology. To investigate this dynamic problem, again a resource cycle perspective is used, but the perspective is expanded to include the dynamics of the different components of metal ecology. As discussed in the previous chapter, the life cycle of a product is dependent on many different, interconnected resource cycles. The metal resource cycles are not only dynamically connected through their combination in multi-components products, but also through the networks of production and recycling processes. These resource cycles - describing the path of all constituting materials/elements that form part of the products - dynamically interact with the technological cycles of products.

The technology cycles describe the cycle of the different technologies employed for the product from cradle to grave: from science, via process design, to the implementation of technology, which in turn leads to a better understanding of the processes (science) as a basis for new process design and development. The resource and technology cycles interact with the societal life cycle, which describes the societal life cycle of a product from cradle to grave, and governs the development of demand for products from society, the rate of product consumption, succession. Figure 1.1 shows the complete life cycle of a product, made up of these interacting cycles; each cycle having its own dynamics. The figure implies that all of these cycles must be attuned, to attain the industrial ecology objectives . Using this ecological perspective, the dynamics of the metal resource cycles are further investigated, and bottlenecks and strategies to reduce the use of non-renewable resources and product related impacts on the external environment are discussed.

4.4 The dilution of metals

From a technological perspective, it can be easily seen that, the technology cycles of pyrometallurgical reactors have a major influence on the resource cycles. They simultaneously perform the chemical transformations necessary to introduce or feed metals back into the material cycle. A change in the feedstock or operation of these networked processes has an effect on other processes upstream and downstream they network, and ultimately on the introduction or feedback of materials into the material cycles. Because of the long lead times and life span of metallurgical processes and waste infrastructure, the dynamics of the related technology cycles is relatively slow: production/recycling routes and technology of metals develop only gradually over time. Consequently, the available knowledge, the employed technologies and the developed network organization determine the possible options for changes in the resource cycles, such as the development of a (new) product. It will be shown that due to the relatively fast dynamics of societal cycles of many products, this particularly becomes a problem when the fraction of secondary raw materials increases (or in industrial ecology terms: when "closing the material cycles").

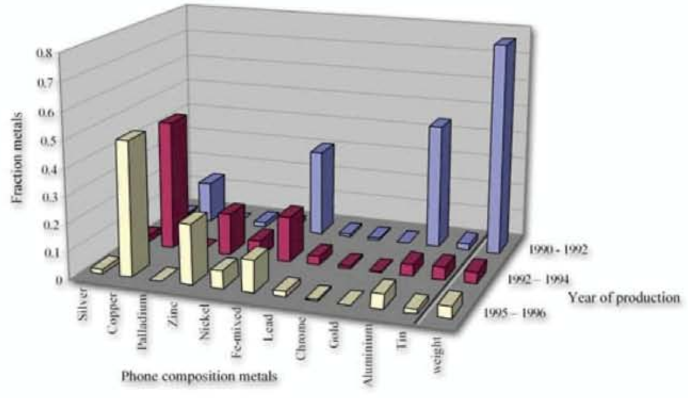

Figure 4.2: Changing composition of cellular phones (source: Van Houwelingen [163])

4.4.1 Interaction with the society cycles

The relatively fast changes in products lead not only to changes in metal demand but also in the supply of secondary resources. Secondary resources (or wastes) often contain many of the elements in the periodic table, and exhibit changing composition and volume, particularly the end-of-life (EOL) products. Part of the metal-containing wastes is generated in the mining, concentration and production of metals. The low metal content in some of the wastes prohibits the economic recovery of the metals in these cases. Metal wastes are also produced in the manufacturing of end products. This "prompt scrap" stays within the factory or production chain, the quality is generally well-known and homogeneous. As a result, this metal can readily return to the production cycle. Waste is also produced as a result of measures to control other environmental problems such as water and air pollution. Some of these increasing amounts of bulk wastes give rise to new problems-examples include sewage sludge and residues from cleaning of flue gases [18]. As an example, zinc in flue dusts can be recovered with current technology (see e.g. Grund [132]), but this is currently done only for materials which contain more than 20% zinc for economic reasons. In particular the materials manufacturing and product assembly further down the resource cycle yield novel types of waste materials and by-products, and thus potentially problems for recycling. Similar to the products themselves, these waste materials exhibit dynamics changes in composition and significant complexity, consider for example the cut-offs in the manufacture of automotive applications (complex alloys or composite, lightweight materials), or off-spec printed circuitry boards. Metals accumulate in the resource cycle through their use in numerous products. These metals become available for further use after discarding of the products as "old scrap". Innovation, competition and fashion create a continuous flux of new products to the market. Thus, unavoidably, the flow of post-consumer solid waste material (and manufacturing wastes) exhibits continuous change with respect to both composition and quantity. The changes in composition of the aggregate of cellular phones produced worldwide illustrate the effect of these phenomena (see Figure 4.2).

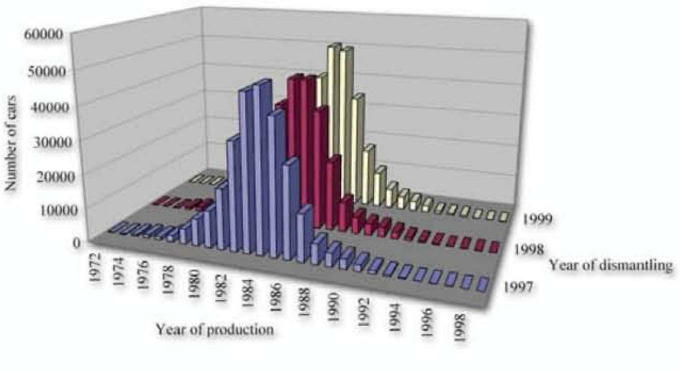

Figure 4.3: Distributed delay between the production and recycling of cars [2]

Not only the compositions of cellular phones, cars etc. per se change, but also the products' complexity. An example of such complexity is the size reduction of electronics (see the decreasing weight of cellular in Figure 4.2) or the increasing use of electronics and computer chips in consumer goods, cars etc. Also material and product innovations lead to the introduction of new physical and chemical linkages; for example, composite materials may include in a single matrix plastics, organic and inorganic fibres, pure metals, metal alloys of diverse composition and doped materials. The inevitable time lag between a product's manufacture and its reception by waste management clearly ranges widely, because the average product life span varies per product and the actual product life span of a product depends on individual consumer preferences and decisions. Figure 4.3 illustrates this effect for cars in the Netherlands [2]. Finally, the total volume of products consumed and eventually discarded, varies as a result of shifting consumer preferences, technology-push, economic prosperity and population. Therefore, waste from end-of-life products has a continually changing composition that is hard to predict.

4.4.2 Interaction with the technological cycle: Metal recycling

From a technological perspective, the waste infrastructure is also an important component in the metal resource cycles because it physically separates the EOL products for the subsequent recycling in metallurgical processes. The objectives of the solid waste management are twofold, however. On the one hand, waste management must concentrate and separate wastes to make subsequent recycling into metals possible and economically feasible; on the other hand, it is an integral part of environmental protection. Improper disposal of municipal waste can result in unsanitary conditions, which in turn can lead to pollution of the environment and to diseases. To date robust, durable infrastructures have been constructed to safely dispose off the waste generated, and minimize impacts on environment and public health, rather than to maximize recovery. To illustrate this, the three main processes in waste management, collection, separation and disposal, as well as the metallurgical recycling to new metal are briefly discussed.

Collection

Ideally, waste is collected in a multi-stream collection system. The separate collection enables subsequent individual treatment per waste category. Thereby, carry-over of impurities is avoided, and better separation can be achieved. Somewhere, however, an optimum must be reached with respect to the number of waste categories collected separately, the cost of the logistics, the implied diseconomies-of-scale in treatment as well as the "willingness" of disposers to separately dispose of their waste. Consequently, only limited separation at the source is possible, and many wastes are collected with the remaining non-separated or remaining fraction.

Separation

In analogy to metal production and recycling, a number of authors observed also similarities between processing of primary metallic resources and secondary metals derived from waste collection [164, 165, 166, 167, 168]. Technologies for recovering metals from waste streams draw extensively on experience gained with processing primary ores [165, 169]. Obviously, pieces of an individual metal are easiest to separate and recycle. The difficulty of separation increases with lower concentrations of metals in the waste, and increasing heterogeneity and complexity. There are two basic strategies to separate and concentrate metals from heterogeneous wastes:

- One is to use a number of different sensors to observe and measure physical properties and remove the commodities with the proper characteristics. Handpicking falls into this category. This type of separation is very selective, and is for example used for extracting valuables from specific demolition wastes. Often, however, the economics of handpicking are unfavourable to separate the bulk of the waste.
- The second strategy is to shred and grind to a fine enough size to liberate the individual components as discrete particles and separate them. The particles can be separated by size (sieving or screening), density difference (e.g. air classifiers, minerals jigs or heavy medium separation), magnetic susceptibility (magnetic pulleys) or electrical conductivity (eddy-current separators). Although the fine grinding can lead to technically difficult separation procedures, the reclaimed products in this way may well be more homogeneous, and in a physical form that is easier to handle [164, 165].

Neither strategy allows full recovery of metals from heterogeneous, continuously changing waste because these rely on physical phenomena only (see example: Non-Ferrous metal separation). Thus, by definition these do not affect or alter the chemical linkage in the material. It is the very downstream processing in metallurgical processes that effects chemical transformations of the waste material.

Cadre 4.1
Non-ferrous metal separation

For the recycling of metals at the desired grades, the effect of impurities in metals waste is critical. It is thus important to process the metal wastes into fractions that are compatible with the specifications of the metallurgical processes downstream the resource cycles. In this process, Eddy-current separation is an important separation step for the separation of non-ferrous

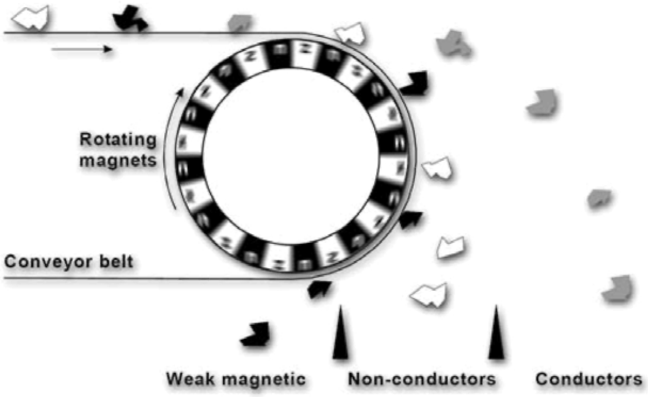

Figure 4.4: The principles of eddy-current separation [128]

metals. In the processing of non-ferrous car scrap for example, an eddy current separator separate the shredded scrap into a weak magnetic fraction, a non-conducting fraction such as glass, stones and plastic, including some small metal pieces, and the remainder of the weak magnetic stainless steel: and a fraction containing the conducting materials or metals (Figure 4.4). The position of the splitter plates determines the composition (or grade) and recovery efficiency of the products obtained.

The particles in Figure 4.4 have different trajectories because they have different rates of acceleration in the magnetic field. This variation is among others caused by the difference in conductivity of the metals, or more precisely, the conductivity divided by the density[2]*. The ratio of conductivity and density differs for each metal: consequently, the acceleration of an aluminium particle will be twice as much as that of a copper particle having the same dimensions. Poor conductors, such as lead and stainless steel, will respond with a slow acceleration to a changing magnetic field, whereas non-conductors, e.g. glass and plastics, will not acquire any acceleration from the magnetic field. In some eddy-current designs, weak and strong magnetic materials will travel with the magnetic drum until the point where the distance between the inside drum and the belt increases. In general, eddy current separators are used in the recycling industry in combination with a heavy media separation plant to improve the grade and recovery of the metal products. The grade and recovery of the metal fractions, however, is largely determined by the efficacy of the size reduction process(es) applied prior to eddy-current separation. The objective of size reduction is the disintegration of different types of mechanically joined materials (e.g. by screw, welding, etc.) to obtain particles of single components. It can be easily seen that when mechanically materials can not be effectively disintegrated by liberation processes, they can not be effectively be separated. The increasing complexity of products thus limits the capacity to separate metals into recyclable fractions (Figure 4.5).*

In addition, chemically bounded materials can not be separated into particles of

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[2] That is at low frequencies of a changing magnetic field. At high frequencies of the magnetic field, acceleration of particles will be dominated by their density.

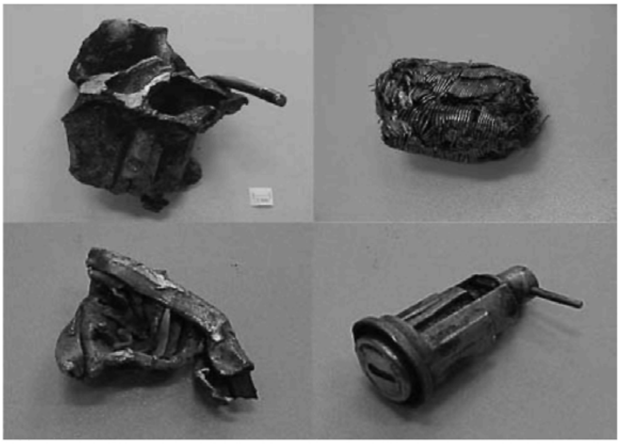

Figure 4.5: Limits of liberation processes: complex mechanically connected components [52]

single components by liberation processes, and thus can not be separated into relatively pure fractions, which for example limits the recycling of composite materials.

Disposal

Most of EoL waste still disposed off with little or no treatment at all. The final disposal of the non-separated waste is limited to a number of allowable operations, including landfill, and incineration. For the disposal of metal containing wastes, incineration and landfilling are the most important options. Environmental impacts have been greatly reduced through among others lining and landfill gas recovery systems, and advanced off-gas treatment systems for incinerators. Landfilling stands alone as the only waste disposal method that can deal with all materials in a solid-waste stream. Consequently, landfills are (still) the most common route for waste disposal, but once landfilled, metals can not be recovered. Although it has been argued that landfills represent the mines of the future, the carry-over of impurities and dilution of metals inhibit feasible economical metal recovery from landfills. Therefore, in order to mine landfills in the future, landfills must be designed for recovery: Wastes must be grouped into different landfill compartments, based on composition, which is currently not the case. In general, disposal processes are primarily built for environmentally sound disposal. Consequently, disposal processes have very limited capacity to concentrate and separate wastes; as a rule-of-thumb, metals should thus be prevented from entering disposal processes to allow their recycling. Incineration can however be an option to concentrate metals from waste with very low metals concentrations, such as for example paints.

4.4.3 Discussion

Metals present an interesting dilemma for industrial ecologists. On the one hand, they are an important source of pollution. On the other hand, metals can be recycled infinitely and considered renewable resources, and would perfectly fit into the closed-cycle industrial ecosystems, or at least in theory. In practice, the accumulation of impurity in the metals cycles (commonly referred to as down-cycling or down-grading) is a major problem, because it limits the usability of secondary metals. It can lead to increased "leaking" in the resource cycles, and inhibits recycling into high-grade metals. The metallurgical research and development developed significant technical infrastructure and knowledge to recycle and deal with a number of elements (see Chapter 2). Waste composition, however, is not determined by the natural occurrence of metals in minerals, but by the product specifications and the capacities of the separation processes in the waste infrastructure. The production system and consumption patterns yield mixed waste materials that contain many different metals. The physical combinations and chemical compositions introduced in products and materials respectively cause carry-over of impurities during recovery, which can result in off-specification secondary metals and alloys. Because in most cases, metal applications require both high quality grades and the absence of specific impurities, their range of suitable applications is limited and a large fraction of the recovered material is useless. Thus, in contrast with common understanding - even in the absence of dissipative metal use and zero growth in demand - for many metals, recovery can not cater for the total metal demand. To produce high-grade metals, incompatible scrap metal concentrations are refused, or mixed with large amounts of primary material that matches the technological capacity to dilute undesired impurities. The current practice of mixing low-quality secondary metals with primary metals does prevent considerable loss of stock in the short-term. The long-term effect of this dilution and down cycling of metals, however, appears to be a neglected issue in industrial ecological studies and strategies: It results in large economic stocks of "polluted" metals that are very difficult to reuse, or at the cost of high environmental impacts, losses of material and energy consumption. This becomes even more important when realized that the desired increasing recovery of metals would imply the recovery of metals from more complex, heterogeneous wastes on the one hand, and smaller quantities of virgin raw materials to dilute the impurities on the other.

4.5 The role of metallurgy in closing the resource cycles

The objective of prescriptive studies in industrial ecology is the control of the metal "organisms", their current organization and their surroundings to realize the strategies outlined in Section 4.2 through optimizing the ensemble of considerations that are involved. The investigation of the dynamics in the metal resource cycles (Section 4.3) showed that industrial ecology concepts, such as closed material cycles, can not be developed from social, political or economic perspectives alone, but must be based on sound technological and scientific knowledge. Without this industrial ecology will remain in the theory and philosophy books. In this section, therefore, the implications of industrial ecology strategies for the different stages (waste management, product manufacture and metal production/recycling) of the resource cycles are explored.

4.5.1 Waste managers: Adaptive waste management strategy

In order to recycle metals from the consumer and other EOL products, the continually changes in waste supply must be dealt with. Using political and economic arguments, Andrews [133] concluded that today's continuously changing waste flows require adaptive waste management. It was argued that industrial ecology provides criteria and a systemic perspective that are helpful in the quest for such improved waste management practice. Little guidance, however, was offered on how to address the technological issues faced in bringing such adaptive waste management into being.

Waste often contains many of the elements in the periodic table, and exhibits changing composition and volume, particularly the end-of-life (EOL) products. These continually changing wastes must be separated and concentrated to make subsequent recycling into high-grade metal possible and economically feasible. This would require flexibility of the waste processing infrastructure, information on composition and volumes of generated waste upstream, and knowledge on the processing capacity downstream (see Example 4.2 below).

Cadre 4.2
Flexible waste infrastructures

The present infrastructure systems for waste management can be labelled "omnivores" [170, 171] that devour the entire diversity of post-consumer waste. These systems have been realized, however, with the objective of waste abatement rather than for (metal) recovery (Section 4.4.2 and Chapter 1). To develop infrastructures with the objective of (metal) recycling, infrastructures must be designed to avoid metal wastes from entering disposal processes, because of their limited metal concentration and separation capacity. Incineration can be an option to concentrate metals from waste with very low metals concentrations as mentioned before. In addition, the chemical composition of recovered metal fractions must match the specifications of metallurgical processes, thus allowing production of high-grade metals downstream. However, waste infrastructures are generally characterized by slow dynamics, or adaptability that results from the scale-of-operations, the related capital-intensity and the size and complexity of infrastructure development projects. Particularly, the centralized disposal facilities in many waste infrastructures cause these slow dynamics of the infrastructures, because of their scale-of-operations and investments in environmental measures. Creating flexible infrastructures to separate continually changing waste flows - but also adapt to changing policy and environmental constraints - is thus a very challenging task. Similar to the cascaded production and decomposition processes in ecosystems - or the cascaded structure of the metal production systems or industrial ecosystems such as Kalundborg- cascaded separation structures in which materials are subsequently stripped from the waste streams, could provide flexibility. This has been suggested in a case study on the Dutch municipal waste system [172]. To avoid carry-over of impurities and improve the subsequent separation and concentration, wastes should be separated at the source. The residues that cannot be recovered must be disposed of in environmentally controlled landfills or incineration plants to minimize the impact (sound waste abatement objective). The opposite is also observed: cascaded separation requires high levels of organization and interdependence, which may partly cancel out the flexibility of such a system [102, 101]. Sagar and Frosch [101] for example notice that the industrial ecological park "Kalundborg seems to have developed locked-in, rigid relationships" and expect that this will be a "problem in the long run since the evolved design of this ecology is based on static optimization", which sometimes is "difficult or expensive to adapt to new conditions". In waste infrastructures, the large-scale, centralized disposal facilities can lead to such a "lock-in" for example [173].

Although it is still unclear to what extent Kalundborg has developed locked-in relationships, considering the flexibility of the system configuration seems particularly important when designing systems for long time spans such as waste and other infrastructures. For the cascaded separation system investigated, this appears not the case: changes in waste composition and quantity are manifested as changes in volume of collected streams. Separate collection, the

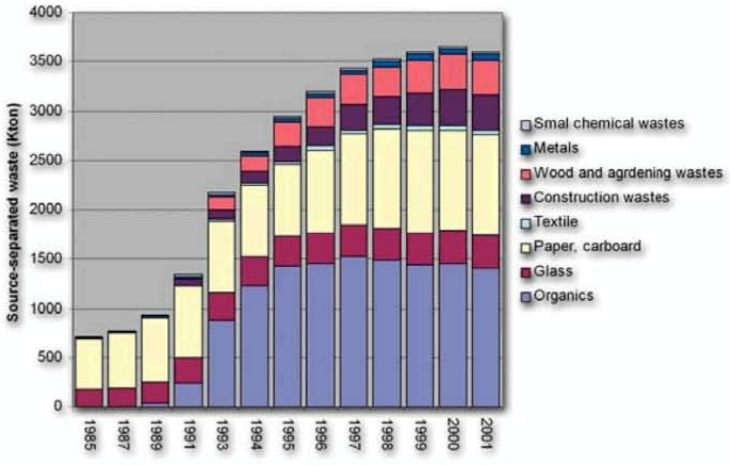

Figure 4.6: Source-separation of household waste in the Netherlands from 1940-1999 [174]

first cascade, can adequately deal with the waste dynamics at limited cost, because it comprises mostly "wheels" and logistics only. The cascaded structure also enables control of the residue composition and quantity downstream. In the 1970s and 1980s, household waste in the Netherlands gradually becomes more complex. Packaging materials (plastics) are introduced. Hazardous materials are found more frequently in household waste, such as batteries, paint, oil, and electronic equipment. The overall grade or quality of the waste for incineration is decreasing. The increase in source separation of household waste (Figure 4.6) partly counters this effect. For instance, the source separation of glass not only produces a secondary resource for glass production, but also improves the quality of remaining household waste. The composition of waste becomes less complex and develops to a biodegradable mixture, which can be composted, and a combustible mixture. Not only for glass, this sequence of events can be identified, but similar trends can be observed for batteries, electronic waste, small chemical waste (e.g. personal care, paint, and oil), paper and biodegradable waste as well. In general, it can be seen that separate collection contributes to the quality of the non-separated household waste.

The cascaded removal of valuables and recyclables, organic and hazardous wastes buffers composition changes in the remaining non-separated waste fraction (Figure 4.7), which in turn may create a favourable climate for investments in waste infrastructure, or in initiatives for the recovery of high calorific waste, e.g. as a fuel for co-incineration and energy generation[3]*. Thus moving downstream the cascade, the capacity-related costs and path dependency increase, but the dynamics of the wastes decrease. This would allow for designing flexible infrastructures. If composition of waste enter-*

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[3] These alternatives also may lead to higher flexibility of the waste infrastructure, because fewer (sunken) investments need to be done in expensive incineration facilities. In addition, these facilities typically have higher energetic/material recovery efficiencies than dedicated waste incinerators. The energetic efficiency of power plants lies around 40%, while dedicated waste incinerators have typical efficiency of around 20%. [173]

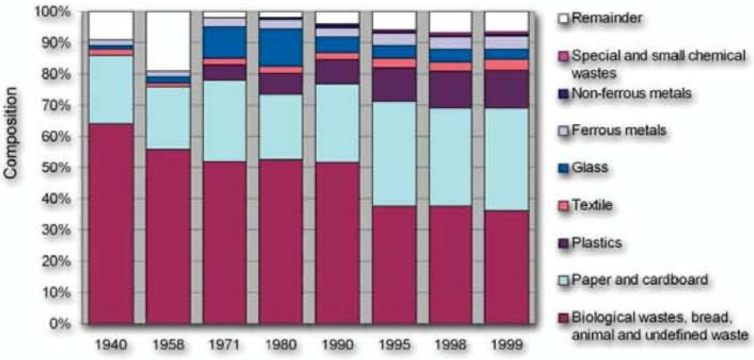


Figure 4.7: Composition of the non-separated household waste in the Netherlands from 1940-1999 [174]

ing the infrastructure is known, residues can be optimized for disposal through incineration, or landfilling. In this way, infrastructures can simultaneously maximize the grade and recovery of metals, and minimize impacts to the environment and public health.

Moreover, it would require improvement of current separation systems. For efficient metals recycling, the chemical composition of the recovered materials in waste collection and separation plants must match specifications of metallurgical processes. If the chemical composition does not match specification, metallurgical recovery rates can be significantly lower, or recovery into high-grade metals is not possible. Therefore, controlling the chemical composition of the materials from waste collection and separation plants through product design is essential to enable maximum recovery of high-grade metals downstream.

Sampling and separation technologies that can better control the composition of the separated fractions are just starting to develop [175]. Figure 4.8 shows an example of such a technology. Such a separation for recovery requires detailed knowledge of the metallurgical system downstream, but also monitoring of wastes upstream. The latter is important to ensure that the wastes follow the necessary separation steps. Given the complexity of many metal-containing products, or the low metal content in others, these separation technologies are not likely to become a full substitute for design for recovery/recycling. Thus, obtaining process compatible scrap metal fractions can not be achieved by adaptive waste management operations alone; it will also require efforts in the product design and manufacturing upstream, and in the metallurgical processes downstream. For metals, the bottleneck for maximum recovery and grade is the further treatment of separately collected waste categories. Controlling the chemical composition of the materials from waste collection and separation plants by correct product design is essential to enable maximum recovery of high-grade metals downstream. In

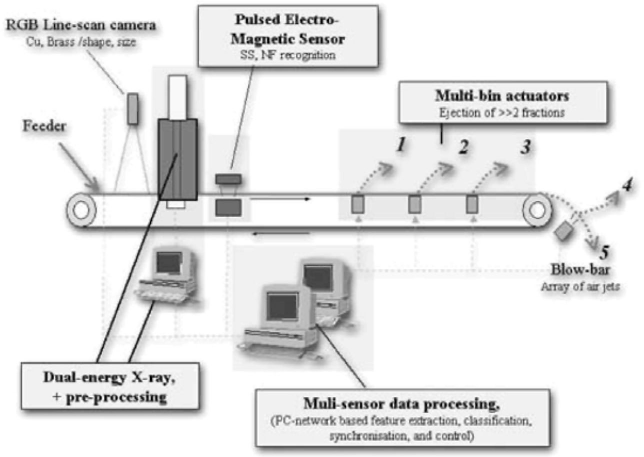


Figure 4.8: Multi-sensor separation technology to control the composition of the separated fractions [175].

other words, adaptive waste management will not relieve product designers and manufacturers of considering the specifications of the metal production downstream to ensure recyclability of their products.

4.5.2 Product designers: Design for metallurgy strategy

To close the material cycles, metal production and recycling constraints must be considered in the process design for at least two reasons:

- Some metals are exclusively produced from the intermediates of the production of other metals, the "carrier" metals. This means that the amount of these metals is constrained by the production of the carrier metals.
- Metal recycling is complicated by the use of products that combine metals that do not naturally occur together. In contrast to the design for recycling involving plastics, a design for metal recycling must not be simply based on the greater use of "mono-materials" but on the use of specific metal groupings. The metal wheel in Chapter 3 showed which metals commonly found together in ores, and thus for which common extraction processes have been developed. It also shows which metal combinations give rise to environmental problems, and/or high costs due to e.g. the need for end-of-pipe measures.

In addition, the neglect of metallurgical considerations in the design of products can lead to errors in estimates of the environmental impacts of the product (see Chapter 5). Graedel and Allenby [12] illustrate the preferred grouping based on a very concise overview of trace metals recovered as by-products. According to them, metal groupings are especially important when a metal is used with a large amount of another metal, such as when steel is plated with cadmium. When the composite material is recycled, the plated metal is generally difficult and uneconomical to recover and tends to be disposed of. Their overview of interdependence of metals, however, is too concise as a basis for process design. Cadmium can be separated together with zinc, and recycled in an Imperial Smelting Furnace for example. The metal wheel in Chapter 3 presents a more comprehensive overview of the metal groupings that can be handled in metallurgical processes. It can be used as a screening tool to select metal combinations in products that are not likely to result in problems for the downstream recycling into metals. Application of the wheel in product design would actually promote the use of multi-metal products; mono-metal based designs are often not desirable from either economic or environmental point of view. Many metals alloys are hard to substitute, and often the alloying elements take a free ride: they are recovered and concentrated at the "cost" of recycling the carrier metal. Elements such as zinc and lead can be recovered from steel arc furnace dusts, and offer no constraints for steel-based product designs. A multi-metal design does not necessarily increase the complexity of the recovery of these metals, nor the cost and/or environmental impact. Moreover, a number of these materials do not have dedicated technical infrastructures, and are dependent on other metals for their recovery or production (the third concentric ring in the wheel). For these materials, a design for recovery is of extreme importance.

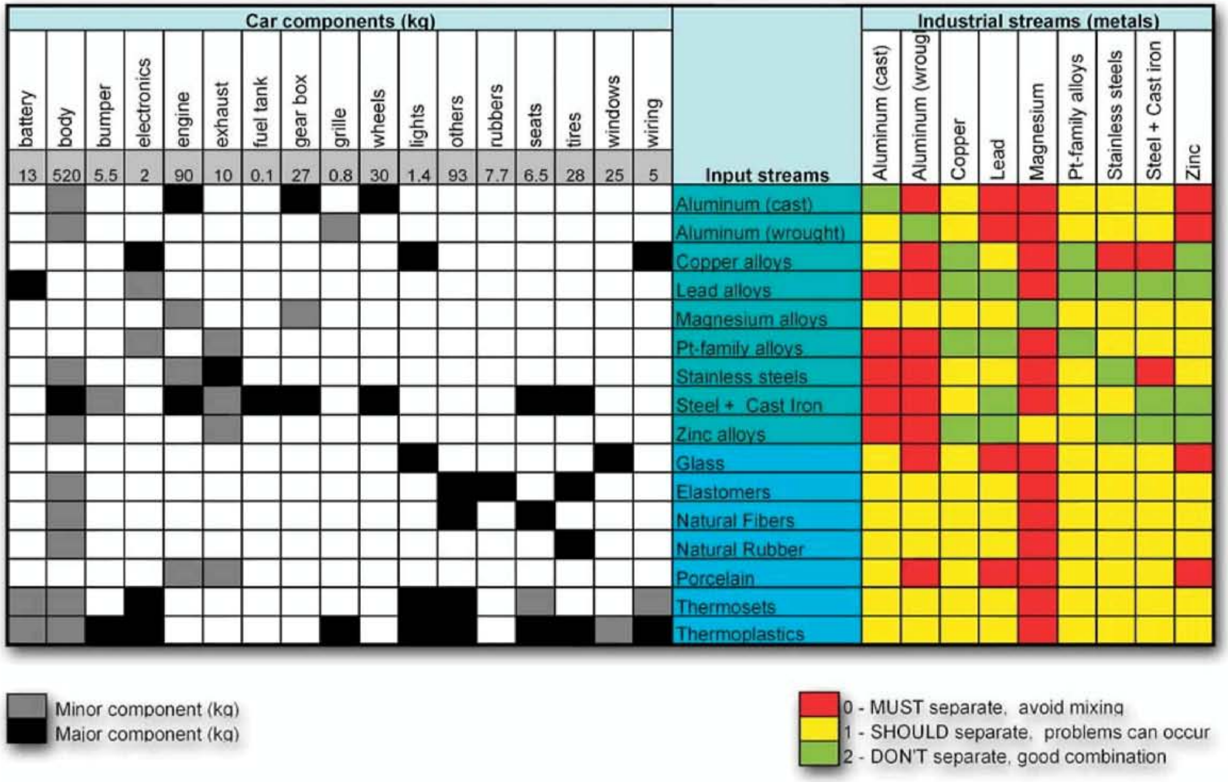
A design for metallurgy is also important as some material combinations must be avoided, such as chemically linked steel and copper that are problematic for both copper and steel production, or the use of iron bolts in lightweight aluminium car frames (see Figure 1.2: the fourth concentric ring). Castro et al. [177] translated these opportunities and constraints in a decision tree for design choices of materials for cars. Figure 4.9 shows which combinations of metals (and other materials) typically occur together in what car components, and which combinations should be promoted or avoided. It shows for example that stainless steel should not be mixed with aluminium or copper, but it can be combined with lead or zinc.

4.5.3 Metallurgists: new approaches to process control and design

Metallurgical reactors play a critical role in closing the metal resource cycles: they simultaneously perform the chemical reactions necessary to feed new materials into the resource cycles, and feed back old materials. If the constraints and opportunities of metallurgical reactors are not understood, sustainability at a bigger scale remains a myth: Metal cycles can never be closed. Sustainability also calls for a radical change in the way the metallurgical reactors are operated, controlled and designed, and thus in the objectives and toolbox of metallurgists (see Reuter et al. [33]). To close metal resource cycles, it must be understood how the operation of the reactors is dependent on other (parts of) resource cycles, and how the operation of one reactor affects the others in the metallurgical network.

Process control and operation

Closing the resource cycles will affect control and operation of metallurgical reactors. Processed must be operated to reduce emissions and accept an increased fraction secondary materials, while simultaneously maintaining the quality of the products, intermediates and residues. The recycling of metals is inextricably bound up with production of metals from ores. Metals are produced through long chains of processes from either primary or secondary resources. In Chapter 2, it was described that to meet increasing environmental and economic pressure, the production chains of the different processes are connected at many points to recover valuable metals typically found in the ores. This provides the metallurgical system with a certain flexibility to deal with variety of different resources. However, the recycling



Car components (kg)																		Industrial streams (metals)								
battery	body	bumper	electronics	engine	exhaust	fuel tank	gear box	grille	wheels	lights	others	rubbers	seats	tires	windows	wiring		Aluminum (cast)	Aluminum (wroug	Copper	Lead	Magnesium	Pt-family alloys	Stainless steels	Steel + Cast iron	Zinc
13	520	5.5	2	90	10	0.1	27	0.8	30	1.4	93	7.7	6.5	28	25	5	**Input streams**									
	▨			■			■		■								Aluminum (cast)	🟩	🟥	🟨	🟥	🟥	🟨	🟨	🟨	🟥
	▨							▨									Aluminum (wrought)	🟨	🟩	🟨	🟥	🟥	🟨	🟨	🟨	🟥
			■							■						■	Copper alloys	🟨	🟥	🟩	🟨	🟥	🟩	🟥	🟥	🟩
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				▨			▨										Magnesium alloys	🟨	🟨	🟨	🟨	🟩	🟨	🟨	🟨	🟨
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	■	▨		■	▨	■	■		■				■	■			Steel + Cast Iron	🟥	🟥	🟨	🟩	🟥	🟨	🟨	🟩	🟩
	▨				▨												Zinc alloys	🟥	🟥	🟩	🟩	🟨	🟨	🟩	🟩	🟩
										■					■		Glass	🟨	🟥	🟨	🟥	🟥	🟨	🟨	🟨	🟥
	▨										■	■		■			Elastomers	🟨	🟨	🟨	🟨	🟥	🟨	🟨	🟨	🟨
	▨										■		■				Natural Fibers	🟨	🟨	🟨	🟨	🟥	🟨	🟨	🟨	🟨
	▨													■			Natural Rubber	🟨	🟨	🟨	🟨	🟥	🟨	🟨	🟨	🟨
				▨	▨												Porcelain	🟨	🟥	🟨	🟥	🟥	🟨	🟨	🟨	🟥
▨	▨		■							■	■		▨			▨	Thermosets	🟨	🟨	🟨	🟨	🟥	🟨	🟨	🟨	🟨
▨	▨	■	■					■		■	■		■	■	▨	■	Thermoplastics	🟨	🟨	🟨	🟨	🟥	🟨	🟨	🟨	🟨

▨ Minor component (kg)
■ Major component (kg)

🟥 0 - MUST separate, avoid mixing
🟨 1 - SHOULD separate, problems can occur
🟩 2 - DON'T separate, good combination

Figure 4.9: Metal grouping in car design [176]

secondary resources often contain material combinations not common in ores, and exhibit far greater dynamics in composition and supply than primary resources. If the recycling rate of metals increases, processes can use less primary raw material to dilute undesired impurities, and have to cope with "new" raw materials and greater variations in their feed. This can lead to the formation of lower-grade products, complex residues streams, and undesired harmful emissions. This inhibits the efficient and environmentally sound recovery of secondary metal resources and affects the economics of the plants that often have tight operating margins. Feedforward and feedback are the two basic control mechanisms in (chemical) process control. The objective in both types of control is to keep values of the controlled parameters at the desired levels. Feedback control uses offsets in the controlled parameters to adjust for disturbances in the input. Feedforward control mechanisms use direct measurements of input disturbances, and based on the anticipated change in control objectives, adjustments are made to minimize offsets in control objectives. When offsets in the controlled parameters are critical, e.g. product quality or critical emissions, feedforward control is preferred. Feedforward enables ideal process control (i.e. no offsets in control objectives), however non-measured or non-modelled disturbances are not compensated for [178]. Chemical process control therefore usually involves both feedback and feedforward control. The simultaneous decrease in emissions and increase in secondary feed will require more feedforward control. Reuter et al. [33] have shown that the distributed chemistry of the (primary and) secondary materials of pyrometallurgical reactors has a significant impact on the reactor/process products, intermediates and residues/emissions and model predictions used for process control. Increased recycling will amplify these effects, and the current practice in process control based on classical models and the experience of human operators[4] may no longer be acceptable at least from environmental point of view. Advanced predictive models of metallurgical reactors are required that allow the selection of suitable resources and adjustment of operating conditions to changes in the feedstock composition. These models must consider the distributed dynamics and chemistry of metallurgical processes; their development should be based on methods to extract useful data, such as data reconciliation (see Chapter 2). A semi-empirical model approach based on these criteria is described in more detail in Eksteen and Reuter [179] and Georgalli et al. [180, 181]. Based on such models metallurgical processes can select proper resources, minimize emissions due to impurities in the feed, or maintain product quality. Because of the variation in the composition of secondary materials, this would require comprehensive sampling of secondary materials. If the compositions are known beforehand, some problematic impurities can be dealt with by adequate action in the metallurgy. The elements nickel, copper, tin, molybdenum, cobalt and tungsten are difficult to remove from steel products. Thus, these must only be present in the waste material processed if desired in the end-product. The presence of nickel, for example, would enable blending waste into an attractive metal source for the production of certain (stainless) steel alloys. In this the way, the down cycling of metals can be minimized. This feedforward resource selection is not a totally unfamiliar concept in metals processing. In secondary aluminium processing scrap is selected (and combined) in such a way that a proper alloy is created, taking into consideration scrap qualities, losses to salt etc. This can be explained from the tight tolerance for impurities in aluminium, and aluminium production processes.

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[4] Human operators learning-by-doing accumulate knowledge and develop mental models of how the processes respond to different raw materials. This illustrates how process control is one of the main drivers for development in extractive metallurgy.

Process design and integration

The efficiency of metal production and recycling is determined by all processes in the metal network, and the flows between the processes (network structure), by the mix of primary and secondary of raw materials and by the demand for metal grades. Traditional engineering approaches to process design, however, tend to focus on modelling and optimization of flows within a process, rather than the flow of materials and energy between processes (see e.g. Douglas [182], Sinnott [183], Allen and Shonnard [184]. Process integration techniques, such as heat- and mass-exchange network optimization, are effective for identifying opportunities for exchange of waste heat and reuse of water and other materials across unit process boundaries. Today these techniques are mainly applied to improving the efficiency of processes or process facilities. Considering the historical development of the metallurgical system (see Chapter 3), a reduction of metal-related emissions, and increase in metal recovery will result in further development of the interdependence between metallurgical processes. Increasing the efficiency of metal production and recycling would therefore call for process integration that goes beyond individual processes or process facilities, and that is based on economic, ecological and technological criteria. Due to the complex interdependence, it is very difficult to determine whether the introduction of a new process (or the phase-out of an old) improves the resource efficiency of metal production and recycling. Without considering the effects on the metallurgical system as a whole, introduction of a new process or other innovations to increase the efficiency of a process can disturb the developed interdependencies, and possibly lead to lower overall efficiencies. For example, replacement of an ISF process with a hydrometallurgical process can reduce emission to air, but can also give rise to problems with the processing of primary iron containing or secondary lead-zinc concentrates, for example. Changes in the production of metals can also affect the recycling metals, and vice versa increased metals recovery can be expected to give rise to problems in metal production. Systems approaches are thus required to put the process design in the context of the larger system. This critical change in the process design approach resembles the change in process design in the 1970s. Engineers began to realize that correctly assembling the process building blocks is just as important as properly selecting and designing individual components (see e.g. El-Halwagi and Spriggs [185])[5]. However, where engineering procedures for the design of individual industrial units are well developed, the problem of determining the best arrangement of these interconnected units is far more difficult. The available tools, which focus mainly on optimization of an individual process, must thus be complemented by systemic assessments of the interconnected metallurgical system.

The development of computer simulation tools allows systematically comparison of different process routes, given economic and environmental constraints (see Figure 4.10). These systemic simulations also help identifying the impact of process introduction/substitution on the operation of the metallurgical system; for example, to what extent the intervention contributes to higher resource efficiency or lower environmental impact of the system as a whole. In the metallurgical (or industrial ecology[6]) literature only few examples of such comprehensive assessments could be found, viz. Reuter et al. [187], Reuter [23] and Südholter

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[5] The discovery of fundamental principles that can guide this assembly led to the concept of "integrated process design" or "process integration", which emphasizes the unity of the entire process. This design approach addresses the big picture first using fundamental principles, and then tackles design details only after the major structural decisions have been made. It assures that the correct details receive attention.

[6] Less comprehensive assessments of the metal production circuits include, for example, Ayres and Ayres [15] or Graedel et al. [110]. Graedel et al. [110] considered on the flows and accumulations of a single metal, viz. copper, in Europe. The purpose of their study was an initial characterisation, i.e. recognition and comparison of the major flows, and identification on the major data deficiencies, rather than providing a basis for improved synthesis of the production routes.

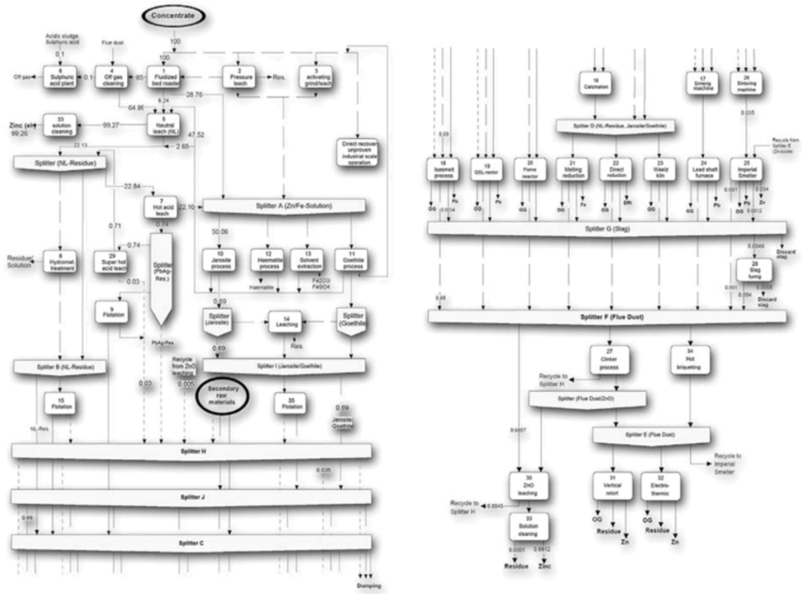

Figure 4.10: Example of computer simulation as a tool to systematically compare different process routes, given economical and environmental constraints [186]. The left flowsheet shows the hydrometallurgical processing of zinc containing materials and the feed of secondary materials to pyrometallurgical unit operations. The right flowsheet shows the pyrometallurgical and hydrometallurgical treatment of intermediate products and residues.

et al. [129]. These studies emphasized mainly the production chains of individual metals, rather than their dynamic interdependence. Sudhölter et al. [129] for instance investigated the synthesis of process routes for the production of zinc based on economic, ecological and technological criteria.

4.5.4 Discussion

It has been illustrated that closing resource cycles is dynamic problem: each stage in the resource cycles has its own dynamics and objectives. The cycles are continuously affected by new product designs, development of legislation and policy, new technology or increased recycling. Growing environmental awareness in society is reflected in an increasing set of environmental standards and protocols laid down in legislation. Technological development, competition and fashion produce continuously changing flow of products flowing through society. Consequently, the resource cycles typically are not in steady state. A sustainable metal metabolism must thus be flexible because in a system of closed resource cycles, as each stage, process and activity is dependent on others but acts more or less independent. The prospects for sustainable metal metabolism are thus determined by society's capability to devise strategies to manage dynamically and globally linked industrial landscape. This will be difficult with our current approaches. Allenby [14] therefore suggests "we need to develop far more power in our systems models and thinking" (see Chapter 2). Because of their complex, dynamic interdependence, this is especially true for the metal resource cycles. To advance towards sustainability, product designers, waste managers or metallurgist must become good system thinkers. Changes at process level affect the dynamics of the larger system, and thus the decision parameters for product designers, waste managers or metallurgists. The role of the metallurgical reactor -a key processing component of the metal cycles- must be understood to assess and address problems in the bigger system, and vice versa. To our knowledge, neither in industrial ecology literature, nor in metallurgy literature models have been reported that considered the dynamic interdependence outlined in the sections above. In industry, metallurgists, metallurgical engineers and process engineers have largely focused on the entity of a catalyst system, a reactor system, or a single plant respectively. The planning and optimization of metallurgical (or refinery- and petrochemical) complexes has been largely the domain of operations research. These designs did not consider the role of a process, or pyrometallurgical reactor in the interconnected metal production system, but typically stopped at the "battery limits". Many of the standard texts of industrial ecology do not address the complexity of metals extraction, processing, metals use and recovery. One of the reasons may be that these texts originate from non metals-technologists. On the other hand, we conjecture that process system engineering may suffer from overspecialization [25] due to their focus on solving problems of limited scope [188]. Resource cycles modelling can be used as the basis for tools that combines industrial ecology overview of the system and can link up detailed engineering models for in-depth information on its subsystems. In contrast to many MFAs, SFAs or industrial ecology studies, this tool must support the communication between industrialists, waste mangers and product designers and represents an attempt to bridge the gap between the holistic view of industrial ecology and analytic view of process engineering. In addition to linking changes in the system to decision-parameters, these models may enable stakeholder assessment, or provide for a forum (or common language) to co-ordinate the different efforts. The description of the metal resource cycles in the previous chapter is a solid basis for construction of such models.

4.6 Controlling the resource cycles

In an ecological perspective, one also looks at the relationships between organisms and their environment. In Section 4.1, therefore, the term "metal ecology" was introduced to refer to the relationships between metals extraction, production, manufacture and recovery processes (discussed in Sections 4.3 and 4.5), as well as the interaction with non-technical, "environmental" factors driving the system, such as economics, policy, legislation and the natural environment (their environment). These "environmental" factors are important because technological solutions alone will not result in a closure of the resource cycles. In industrial societies, economic markets are the basic control mechanism by which available resources - the term resources is used here in the widest sense, including financial resources, materials resources, capital goods etc. - are allocated to the different processes across system levels, dependent on the societal demand for the services/products these processes produce. The control mechanism co-ordinates different processes to produce the desired services/products across all systems levels and throughout all stages in the resource cycles. In many textbooks on economics (e.g. Baumol and Blinder [189]) one can read that the "invisible hand" of the market allocates resources efficiently. Without any guidance from governments, free market economies have achieved unprecedented levels of outputs, productive efficiency, variety in available consumer goods and general prosperity. However, the market mechanism has also weaknesses, among others its ability to cope with externalities (such as the environmental impact of economic activities, which has lead to concerns about the sustainability of current market economies. See also Chapter 2). Because of the market inability to cope with externalities, governments have found it appropriate to intervene through policy and legislation, and create additional incentives, restrain or even prohibit certain activities. This section investigates the potential of markets/economics, policy and legislation to the close material cycles, using the EU waste legislation as a case. Because of the environmental impacts associated with waste management, different regulatory regimes apply for wastes and virgin or primary resources in the EU. Consequently, EU regulation largely shapes the technological choice for waste disposal, incineration, or recovery options.

Cadre 4.3
The need for integrated waste policy and legislation

The goals for waste policy and legislation are simple: stimulate waste prevention and recycling, and minimize impacts of waste processing. This has led to the so-called "waste management hierarchy" that is the basis of the EU waste policy and legislation (EU [190] the "Waste framework" directive). Waste should be prevented as much as possible. If waste can not be avoided it should be recovered (reused, recycled, or "thermally recycled"). Final residues that can not be prevented or recovered must be disposed of with as little (negative) environmental impact as possible. In the western world, policy and legislation have been particularly successful in controlling the pollution of metal recycling and waste disposal processes, typically resulting in end-of-pipe solutions. Wernick and Themelis ([169], after Frosch [191]) observe that while U.S. regulations have been "successful in controlling air and water emissions from point sources", they have been far less successful in the development of policy and legislation "that serve to protect the environment as well as encourage optimal metal recovery". This appears the case for the European waste legislation as well. EU waste legislation in many countries raised standards, which resulted in a better regulation and monitoring of potentially harmful activities, rather than in effective control of the growth in waste generation (preven-

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tion), or stimulation of recovery and recycling and reduction of disposal [192, 18]. One of the reasons is that waste management is a complex, politically loaded and emotionally charged issue that is neither well structured nor well understood [193, 194, 192]. The success or failure of the EU waste policy and legislation depends on a complex partly market-based system governed by different local, national, and international regulations, the capacity of treatment facilities and the price structure between treatment forms and between nations. In theory, the process of developing legislation should provide for examination and balancing of scientific evidence and policy goals. There are both conceptual and practical difficulties in collecting factual data and linking them in a meaningful way to the impact of legislative and policy instruments. The composition of waste flows and the capacity of processing facilities are not well known. European waste statistics are still based on inconsistent approaches to the categorization and listing of the types of wastes. Hardly any information is available on the capacity for reuse and recycling of different wastes and assessment of that capacity is complicated by the fact that many recyclable materials - metals in particular - are traded on the world market [18]. Without feedback on system performance through consistent statistics on waste generation, it is difficult to determine the effectiveness of policies and legislation on disposal and recovery. Consequently, there is a need for structuring the problem of waste management, and examination of the effectiveness of the traditional regulatory, market-based incentives, but also for new policy instruments such as voluntary approaches (see e.g. O'Rourke et al. [71], Harrison [195] and Andrews [133]). In addition, the fragmentation in the development of policy and legislation complicates acquiring a coherent, transparent legislative framework [13]. Even within EU member states, the development process is still often fragmented across many governmental bodies, media of pollution, and/or stages in product life cycles. As a result Tromans [192] observes that the apparently simple principles of the waste management hierarchy gave rise to "a body of EC and national law that is notoriously difficult, even for specialist lawyers and which - even for such lawyers- makes little sense in terms of some of its points of detail." Waste policy and legislation rigorously define wastes and their sources to avoid environmental problems, but at times severely limit their transport, reuse and recovery [196, 197, 111, 13, 198]. Perhaps more important, the lack of a clear, consistent regulatory framework also inhibits effective regulation and co-ordination of the different activities and processes involved in prevention, recycling and disposal of waste. From an industrial ecology perspective, the main distinction between point source (or emission) control on the one hand, and preventing waste generation and stimulating recycling on the other, is that the latter two require co-ordination of the different activities and processes involved. When waste is considered an "emerging attribute" of materials, substances and products (see Chapter 1), waste management becomes a wider subject than waste treatment alone. It follows that many solutions to waste problems can not be found in waste management itself but must be looked for in the processes upstream and downstream. Neither can the challenge of increasing waste quantities be solved in a sustainable way by efficient waste management and recycling alone. The recycling of metals is a function of the extraction and production of metals, the manufacture of products, consumption activities as well as waste management. Thus to stimulate recycling of waste, it must be analyzed and handled as an integrated part of total material flow through the global society (e.g. EEA [18]). It thus requires co-ordination of the different activities and processes in the resources cycles, and calls for integrated policies and legislation.

4.6.1 Integrated control of the metal resource cycles

Integrated policies and legislation address the problem of resource management, rather than waste management alone. The required co-ordination of the different activities and processes in the resources cycles to minimize losses is a dynamic problem. The industrial ecology metaphor is a convenient way of structuring the dynamic problem of waste/resource management. Lowe et al. [13] argue that the metaphor of industrial ecology is particularly powerful in terms of ecosystem interaction and dynamics; natural ecosystems are "tested" sustainable systems, evolved over millennia and flexible in the face of change[7]. The dynamic stability of ecosystems is a result of their organization as bottom-up or self-organizing feedback systems (see Chapter 2). The resemblance of self-organizing capacity of (competitive) markets with the self-organization (or "autopoeisis") of natural ecosystems through decentralized processes, may explain the sympathy for market as co-ordination mechanism in prescriptive industrial ecology studies. To use the self-organizing capacity of markets, legislation and policies must provide for incentives and restrictions without inhibiting industrial change and innovation. In the EU, some of these incentives and restrictions have already led to the development of legislation. The directive on the landfill of waste has laid down objectives for the landfilling of waste, and should increase recycling as a consequence. The European Union's proposed Integrated Product Policy (IPP) seeks to stimulate demand for greener product lifecycles (EC Commission [199]). Recent initiatives that lay down concrete objectives for recovery/recycling at the product manufacturers are the directive on packaging, end-of-life vehicles and wasted electric and electronic equipment. Much work still need to be done before waste is regulated as an integrated part of total material flow through the global society. In the next sections, waste management is structured from an industrial ecology perspective.

4.6.2 Metal resource cycles as self-organizing feedback systems

Increasing the recycling of waste and closing the resource cycles require the simultaneous control of a great many processes and activities that are connected in a network of mass and energy flows. Many of these network relationships are determined at process level. The match between the operational knowledge, and technological capacity of processes and physical and chemical composition of resources, determines its value as a resource or its hazard to the environment. Because waste composition and the industrial recycling capabilities are not well known by regulators, top-down control has resulted in the lack of clear definitions on key terms, and the imposition of wide and open-ended objectives, which leads to further complications due to differences in interpretation internationally. A typical example is the definition of waste and recovery in the regulation of cross-border transport of waste [196, 173, 7, 200, 192]. The top-down policy and legislation, set out to minimize the hazards of waste transport, may actually discourage the use of secondary resources. Because the match between process capabilities and waste composition can be better determined at process level, regulatory efforts should use the decentralized knowledge of industrial processes. In other words, it should be based on bottom-up control and the self-organizing capacity of primary and secondary resource markets. This will be illustrated in Example 4.4 below.

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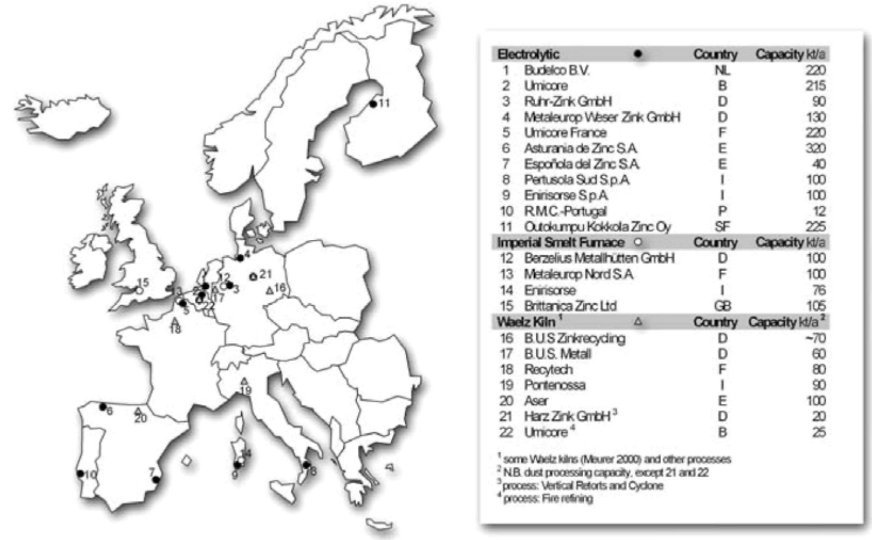
[7] Many other industrial ecologist also stress the importance of dynamic perspectives in IE studies (see section), and draw on ecosystems as inspiration for industrial systems (see Chapter 2: e.g. Allenby [14], Ehrenfeld [84])



Electrolytic ●		Country	Capacity kt/a
1	Budelco B.V.	NL	220
2	Umicore	B	215
3	Ruhr-Zink GmbH	D	90
4	Metaleurop Weser Zink GmbH	D	130
5	Umicore France	F	220
6	Asturania de Zinc S.A	E	320
7	Espoñola del Zinc S.A	E	40
8	Pertusola Sud S.p.A	I	100
9	Enirisorse S.p.A	I	100
10	R.M.C.-Portugal	P	12
11	Outokumpu Kokkola Zinc Oy	SF	225
Imperial Smelt Furnace ○		**Country**	**Capacity kt/a**
12	Berzelius Metallhütten GmbH	D	100
13	Metaleurop Nord S.A	F	100
14	Enirisorse	I	76
15	Brittanica Zinc Ltd	GB	105
Waelz Kiln [1] △		**Country**	**Capacity kt/a [2]**
16	B.U.S Zinkrecycling	D	~70
17	B.U.S. Metall	D	60
18	Recytech	F	80
19	Pontenossa	I	90
20	Aser	E	100
21	Harz Zink GmbH [3]	D	20
22	Umicore [4]	B	25

[1] some Waelz kilns (Meurer 2000) and other processes
[2] N.B. dust processing capacity, except 21 and 22
[3] process: Vertical Retorts and Cyclone
[4] process: Fire refining

Figure 4.11: Location and capacity of zinc processes in the EU

Cadre 4.4
Cross-border transport of waste

The very qualification of a material as waste or secondary raw material has many consequences on what is allowed or not, what administrative procedures apply to its transport, export or processing, and what costs will be incurred [198]. The problem is that the present qualification waste has no direct link with the potential of the waste to be recycled, or the impact of the waste treatment. Products, substance or materials become waste, when they are discarded, or when they are intended, or are required to be discarded (EU [190] Waste framework directive). This inhibits the recycling of some metals because of the rigorous processing requirements, and the more onerous permit and transport requirements for secondary materials than for primary, but also because of the negative image conferred to the material. In addition, the differences in interpretation between member states or internationally may yield divergent standards for metal recovery (resulting in "unfair competition" or barriers to trade) or restraint transport of waste to suitable recycling facilities in other countries. Figure 4.11 shows that because zinc processes are distributed around Europe, metals often must cross national borders to be recycled.

In the EU, the regulation [201] on the shipment of waste is based on "red, amber and green lists". Wastes are categorized according to their hazard: from non-hazardous waste (green) to hazardous waste (red). This categorization, and its intended use (recovery or disposal), *determines the conditions under which the waste may be transported. Because of the difficulty of labelling products as waste, and processes as recovery operations, the treatment of unassigned wastes leads to different interpretations among member states, and even institutions within the EU [192]. National authorities can assign (as is the case in the Netherlands, for example) mixtures of components that individually are listed as green or amber, and are not specifically assigned to any of the lists to the red list (hazardous waste)*[8]*. Consequently, it is difficult for the metal recycling companies to see the trees in this dense regulatory forest, due to the complex categorization of waste, recovery operations, and national policies; and the ambiguous transport requirements discourage recycling. The problem is that the actual hazard or value of wastes as a resource is determined by the match between the specifications of the process with the (physical and chemical) composition of the waste. The diversity in waste and metals recycling processes complicates developing a more consistent approach to the categorization of products as waste in standardized list, or processes as recovery operations. Because of the continuous variation in waste material combinations and volumes, not all waste substances, materials or products can be included in the list, and this rigid top-down regulation restricts and complicates the transport and, therefore, the recycling of metals. In ecosystems, the exchanges of nutrients between organisms are maintained through self-organizing process as well, not top-down control [13]. By analogy, a shift to decentralized or bottom-up control through policy and legislation could provide more freedom for the processes to select and transport suitable resources, and thus a more stable supply of resources. Bottom-up legislation could be based on their environmental impact (e.g. operating licenses), rather than on restricting the flow of wastes based on standardized lists. Processes are allowed to use different resources as long as they obey strict environmental limits and standards, and obviously meet specifications of the product manufacturers. Because emissions and residues are determined by the match between feedstock and process capacity, this will force metal producers to judge continuously secondary resources based on their hazard and their value for the process. The obvious advantage of this form of decentralized control is that it builds on the decentralized knowledge stored in individual processes to select resources that are compatible with the required overall system performance.*

Relationships between activities and processes in the metal resource cycles are maintained through economic markets that can be viewed as self-organizing feedback systems. A balance in positive and negative feedback loops provide markets with an element of stability. Positive feedback stimulates certain behaviour, whereas negative feedback curbs certain activities. If for one reason or another, a metal becomes less available, its price rises. This causes a number of actions to occur which limit the rise, and or affect the production of the metal. Higher prices stimulate people to use less of a product (negative feedback). Higher prices also encourage metal producers to increase process capacity based on existing technology, or find new ways through research on alternatives (positive feedback). The dynamic performance of the industrial system as a whole is controlled through "economic" selection: the sum of positive and negative feedback. If a process becomes less economically "fit", the technology is less likely to be reproduced in new processes. Consequently its population declines, unless it is able to adapt. Too strict "economic" selection, however, may offset the balance between the "static" productivity and efficiency of the industrial system and its "dynamic" flexibility or adaptability to cope with changes in material or energy flows. Because environmental impacts are difficult to express in monetary units (so-called economic externalities), the negative feedback from the environment perceived by industrial activities is typically much smaller than

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[8] A typical example is electric wiring: individually plastic and copper are on the green list; however, electric wiring that consists of plastic and copper is treated as hazardous waste, although it can be very well recycled (see for example MRF [202]).

the positive feedback of the economic profits resulting from the activities. Therefore, the goal for environmental policy and legislation must be to strengthen the negative feedback loop by measuring and monitoring the environmental impacts of flows into the environment and internalizing these impacts into economic theory and practice. The problem of "dilution of metals" described in Section 4.3 can be considered a problem of balancing feedback loops. A key principle in industrial ecology is the cyclic use of materials. In society metal retention - that is the ongoing use or availability of metal in the economy, between the life cycle stages of resource extraction and final disposal back into the lithosphere - is finite because of the limited grade of secondary (recycled) metals. Currently, metals are maintained in their utility through the addition of high-grade primary (virgin) metals, bringing the concentration of impurities in the metals produced to desired levels. This mixing with high-grade primary metals keeps these recycled metals in the cycle. Consequently, there is no negative feedback on the composition of products. The selection of metals for products is primarily controlled by the positive feedback from the economic benefits of using the specific properties of the many different metal alloys and combinations. Long-term, this practice of dilution of the undesired substances prevents a closure of the material cycles, whereas recovery without dilution will reduce the quality (or quantity) of recycled metals. Simultaneous minimization of environmental impacts, increase in recycling and avoidance of metal dilution, will call for integrated legislation and policies (see Sections 4.5 and 4.3) The "extended producer responsibility" can strengthen the negative feedback loop in selection of metals for products by making manufacturers responsible for the recycling of their products. Somewhere a balance must be found between the protective constraints of legislations, and the freedom of industry to adapt. Metallurgical processes need room to adapt and innovate, in order to achieve (or exceed) the required legislative requirements and desired product grades under dynamic conditions. Process boundary conditions continuously change due to fluctuations in the demand for metals, the supply of primary and secondary raw materials or the development of policy and legislation. Positive and negative feedback mechanisms in markets must therefore not select on environmental efficiency and economic productivity alone, since this could offset the dynamic balance with flexibility of the metal production systems. If the goal of legislation is environmentally sound recycling rather than dilution of metals, legislation can not fix all degrees of freedom of process operation: restrict the supply of secondary resources, prescribe the use of the best available technologies, and set limits to emissions and residues. Rather it must select a critical set of process outcomes. The puzzle of bottom-up control is thus finding a set of process constraints that lead to the desired industrial performance but do not restrict industry to adapt and innovate. This is further illustrated in Example 4.5 below.

Cadre 4.5

Best available technology

Waste/environmental policy and legislation are often perceived as an inevitable trade-off between the social benefits of mandated environmental standards and industry's private costs of prevention, control, and clean-up. According to Porter and Van der Linde [203, 204], this perception neglects the dynamic character of industrial innovation in response to environmental pressures. They argue that environmental regulations can actually benefit competitiveness, if they allow industry to change and innovate. In this way, industry can simultaneously increase resource efficiency and enhance their competitiveness. Such policy and legislation must not be based on top-down prescription of technical solutions, which has been one the most limiting aspects of environmental regulation, but on process outcomes [13, 203, 204, 196]. If a process *or industry is not locked into a certain answer, it has the room to adapt and innovate, and to achieve or exceed required performance. This bottom-up type of legislation and policy offers industry a more degrees of freedom to respond to changing regulation or changes in other process conditions. The problem is how to measure and enforce process "outcomes" without prescribing technological solutions. The EU IPPC directive (EU [205]) lays down that emission limit values, parameters or equivalent technical measures should be based on the Best Available Technologies (BATs), without prescribing the use of one specific technology and considering the technical characteristics of the installation concerned. Enforcing the directive is difficult, because the best available technology alternatives are likely to be plant level specific, if not site specific. Older pyrometallurgical furnaces generally have higher energy consumption and/or emissions. This easily leads to the assumption that using these furnaces can not be regarded as employing best available technologies. Often however these furnaces are integrated into process plants or used by other plants (see Chapter 2 for examples), and thus can not be considered independently of the other processes. They can add specific tasks or capacities to the process plant as a whole, such as the production of high-grade metals from complex metal resources, co-recovery of metals which recovery otherwise would not have been feasible, or handle of critical residues from other processes. At system level, the resultant diversity in metallurgical process enables effective recovery of different resource mixes, and recycling of residues. To minimize the potentially negative impact of environmental protection on industrial competitiveness, implementation of BAT policies requires solid understanding of the industrial system. First, BAT policies can hold back innovation, as technological innovation is generally faster than legislative development. Second, without proper consideration the role of a process in the metallurgical network, implementation of BAT legislation could also render critical processes in the metallurgical network unprofitable. It in turn can restrict the use of metal in different products, or inhibit the recycling of certain metal wastes. This explains why Porter and Van der Linde [203, 204] conclude that in order to balance the protective constraints of legislations and the freedom of industry to adapt, industry should participate in the setting of environmental standards and the development of BAT policies from the beginning to feed the necessary technological information into the decision-making process. In addition, the regulatory process should become more stable and predictable, so that its expected outcome can be included in the planning of product development, technology, marketing and organizational support.*

In addition, there are also limits to the self-organization activities and processes in the resource cycle through feedback. Feedback control is reactive, which means that when offsets in the control objectives are measured, actions are taken to minimize the offsets. Moreover, even if positive and negative feedback loops are in balance, feedback systems can become unstable. Many natural, industrial and economic feedback systems have delays in adjusting and consequently are prone to "hunting". Due to the delay, the negative feedback corrections may come too late, and give rise to a series of over-corrections, a phenomenon commonly known as hunting. In Chapter 2, it was argued that the more variables fluctuating in ecological networks, the larger their capacity to adapt to changes in environmental conditions. In economic systems, these oscillations in network variables (e.g. material and energy exchanges, process populations) may be unacceptable. Due to the operation-of-scale, the sunken investments, the long lead times and economic life spans, oscillations in process populations are limited. Section 4.3 showed that oscillations in flows between processes arising from the fast dynamic in societal cycles are a problem when these dynamics are faster than the technology cycles of process innovation. As a consequence, they lead to increased emissions, residues, and/or decreased product grades (metal dilution). Controlling these oscillations becomes even more essential for two reasons: On the one hand, because the development towards closed resource cycle will lead to more feedback through the system; this increases the chance of oscillations. On the other hand, the closer industrial activities approach the carrying capacity of the planet, the higher the hazards of these oscillations (i.e. the faster increases in emissions and residues (irreversibly) affect the function and viability of ecosystems).

4.6.3 Feedforward control of resource cycles

To stabilize the dynamics in the resource cycles and minimize emissions and residues, industrial policy and legislation should be based on more feedforward type control of the system. In process control, feedforward loops allow "ideal" control even when systems exhibit delays: no offsets in the control objectives (see Section 4.5.3). The delays provide time to adjust process conditions to disturbances. Although not often recognized as such[9], even in nature feedforward is an important control mechanism that stabilizes the ecosystem dynamics. Although feedback is a process of reaction, feedforward expectations are often part of the feedback loops in nature. These expectations based on previous experiences intuitively affect future experiences: If for example an animal has eaten food that is hard to digest of gave other problems, it will adjust its diet to avoid these problems. A first requirement for feedforward control is a predictive, dynamic model of the controlled system. In ecosystems, the feedforward expectations use the mental models of how individuals see their environment. These mental models in turn influence the environment because individuals then base decisions on these models. According to Capra [10] this process of anticipation - or cognition as he calls it - is common to all organisms[10]. The predictive model is linked to the physical development of organisms: The physical structure of organisms is "a record of previous structural changes" which in turn are a reflection of its experiences. The requirement of predictive models for feedforward control explains why in industrial systems, much of the environmental policy is necessarily reactive. The world is too complex to predict the environmental consequences of technological, policy or legislative changes. Specific activities and processes, however, can be modelled. The second requirement for feedforward control is that disturbances must be measured beforehand: Disturbances that are not measured can not be compensated for. Predictive models of processes can be developed that enable feedforward control (see Section 4.5.3), if processes can measure possible disturbances beforehand. Each process must receive information that should be tracked upstream and downstream in order to timely alter the operation, when these "signposts" reach critical levels that require action. To stimulate feedforward self-organization, policy and legislation can help develop, introduce and standardize these signposts. Obviously, the earlier in the metal life cycles changes are measured the better the system can respond. This is particularly true for large-scale systems, such as waste infrastructures, that because of their large inertia require considerable time to adjust operation. By careful tracking of consumption patterns and waste disposal per category, one can anticipate changes in waste composition and quantity and change the frequency of collecting, building or depleting stocks and gradually increase or decrease processing capacity. In this way, the life span of products buys time for metallurgical processes and/or waste processors to react to changes in product

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[9] In Industrial ecology, ecosystem models are often based on the principles of natural selection and feedback. Interestingly, the IE strategies, such as extended producer responsibility and design for environment strategies, can be considered feedforward concepts. The strategies seek to reduce the impact of a product using some model of the industrial activities to consider the disposal, reuse and recycling options arising from the designed products. Ideally, this model should present available technology for processing materials, gaps in the available technology and constraints of these technologies as input for the design.

[10] Cognition is not limited to organisms, but a property of all life. In this context, ecosystems can also be considered cognitive systems; their reaction to change is shaped by the available diversity of organisms. Although the cognition itself is a feedback process, it gives rise to another basic mechanism: feedforward control.

manufacture by modification of existing, or development new (pre-treatment) processes. Also for other disturbances such as changing legislative requirements of processes, e.g. process temperature, residence time and emissions, or increased energy recovery, it is important to receive this information as early as possible.

4.6.4 Hybrid Feedback and Feedforward control

Tibbs [206] already argued that industrial ecology should be proactive (feedforward) not reactive (feedback). It should be initiated and promoted by industrial concerns because it is in their own interest and in the interest of those surrounding systems with which they interact, not because it is imposed by the feedback one or more external factors. Industrial concerns to date initiated and promoted and additional control through policy and legislation is necessary. The problem of feedforward control is that non-measured or non-modelled disturbances are not compensated for. The problem of feedback control is thus to define a critical set of process outcomes. Due to the complexity of resources cycles, its control must be hybrid: both feedback and feedforward. This can be illustrated using the concept of extended producer responsibility [207] for instance, which contains both feedforward and feedback elements:

- Feedback: the responsibility (physically and/or economically, fully or partially) is shifted upstream to the producer and away from municipal waste managers, and metal recyclers. In this way, the consequences of the product recyclability are led back to the manufacturer, providing positive or negative feedback on the design activities.
- Feedforward: incentives and objectives are provided to producers to take environmental and recyclability considerations into account in the design of the product. EU regulation aims to achieve 85% recovery of cars in 2008 [9] and 95% in 2015. This is a way to feedforward the constraints of recovery in the design of products, by setting minimum recycling percentages of products.

The objectives for the self-organizing capacity can only be defined based on some (predictive or feedforward) model of the system. In the definition of the objectives, it is essential to determine at what point in the recovery or recycling process it can be properly claimed that a waste has been recovered or recycled. Recycling or recovery objectives can refer to the percentages of the car materials that enter the metallurgical recovery process, or to the amount of metal that find its way into new products. This distinction is important because how the materials are delivered to the metallurgical process has great influence on the amount of metal containing products that can be recovered as high-grade metal. In case of the latter interpretation the objective of the EU seem unrealistically high, particularly considering the trend towards greater complexity of cars, and increased use of composite materials. Following the first interpretation optimization of the amount of material separated from the vehicle may, in fact, even lead to a reduction of the overall recycling, or contribute to the dilution of metals (see Figure 8.4).

The concept of feedforward control illustrates the role of descriptive approaches in the coordination of decision-making across system levels. They provide "snapshots" of parts of the physical economy and connect the flows of mass and energy through the economy to social, environmental costs, or other decision or performance parameters. If properly constructed, these models allow policy-makers, legislators, but also products designers or engineers, to anticipate and minimize environmental impacts. Predictive, quantitative models of the system are required to promote feedforward control of the system. An example of such a feed forward model approach is presented by Van Schaik et al. [51]. Her model - based on the dynamics at process and product level - provides a basis for improvement of recycling legislation. Such dynamic modelling can show the effect of changing lifetime, weight and composition of cars on the recycling rate of End-of-Life vehicles (Elves). As such, it can support a design for recycling, optimization of the dismantling, mechanical separation and pyro/hydrometallurgical processes involved in ELV recycling, and thus the establishment of proper legislative incentives. As said before, the world is too complex to predict the environmental consequences of technological, policy or legislative changes. Even if there does not exist - and maybe there never will exist - an integrated model capable of describing such changes, striving towards such a model structures problems and gives valuable insights about how the processes interact and how this might effect the environment. This knowledge then can be used to include the proper stakeholders in the development process of legislation and policy. This is important because including the proper stakeholders brings a knowledge base into the processes, which may lead to better a feedforward model. Direct involvement of industry can ensure that technical complexities of the legislation are not overlooked, and can assist in formulating policy alternatives. Finally, industry should participate in the setting of environmental standards from the beginning to be able to include these in planning of process development, technology, marketing and organizational support.

4.6.5 Discussion

The goals of reduction of emissions and increasing resource efficiency as a long-term solution present a tremendous challenge, and will result in complex non-linear systems. The main problem is - as Allenby [14] pointed out- that the degree and kind of controls and knowledge that such a complex, non-linear systems would imply are currently beyond the state-of-the-art. Where simple systems are intuitively "understandable", many aspects of complex systems are difficult and counterintuitive, and frequently are illustrated only by the behaviour of properly constructed quantitative models. These quantitative models are closely linked to feedforward control, or the forward-looking research and practice in the field of industrial ecology. In order to effectively cope with dynamics in a complex interdependent system, both feedback and feedforward control strategies are essential for policy, process design and process control alike. When offsets in the controlled parameters are critical, feedforward control minimize offsets in control objectives. Where direct measurements of input disturbances, or anticipation of change in control objectives is not possible, feedback provides a second control mechanism. To advance towards sustainable metal metabolism through increased feedforward control, product engineers, waste managers and regulators must become good systems thinkers; they must be able to link the dynamics of the global metal metabolisms to the dynamics at process level, and vice versa. Few product engineers, waste managers and regulators will have a good overview of the operation of the metal metabolism as an interdependent system. In order to co-ordinate actions in the metal metabolism, a model of the dynamic, interconnected and interdependent metal cycles must be developed that bridges the gap between "holistic" models of industrial ecology, and detailed models of process engineering. This will be further discussed in the next chapter. The development of such models is essential to meet the industrial ecology goals for two reasons. First, construction of such models will at least lead to an understanding of the system dynamics, or structures problems. In such a way, the effects of changes to the technological infrastructure (e.g. new legislation, product designs, waste recovery operations or metal production processes) can be estimated, and possible bottlenecks identified. Second, such models would be suited to initiate further development of the products, or the production network by the stakeholders involved even if not all dynamics can be adequately captured. As such, the model could also assist in making the complex metallurgical knowledge available for waste management, policy and product design.

4.7 Summary

Implementation of industrial ecology leads to increasingly complex, interdependent systems. Because of their critical role in the metal resource cycles, a solid and detailed understanding of metal production and recycling is essential to *assess* and *address* the problems of industrial ecology strategies with respect to metals. A further development towards a reduction of metal-related emissions, and increase in metal recovery is likely to result in further development of the interdependence between processes, and stronger feedback through the metal cycles. Because of this interdependence, increased recovery can lead to contamination of stocks of metals in use, and therefore to degradation of the metals capacity to be (infinitely) recycled. Therefore, a sustainable metal metabolism is shaped by our ability to effectively control this infrastructure, and understand the changing role/requirements of the players in the metal ecology. Industrial metals represent a network of globally linked materials that can not be studied usefully in isolation, but require an integrated approach for its understanding and improvement: The technical characteristics of the installations concerned, and their roles in the dynamically interlinked production and recovery system linked to environmental performance. Only through a "concerted" effort can society approach closed material cycles. Product manufacturers must design products for the environment, deliberately considering the recovery of the products after use. Waste processors must optimize the source separation, and further develop separation plants. Industry must develop better technology to isolate and recover maximum value from metals in waste streams, and deal with changes in inputs. Governments must develop regulation that promotes recovery, and institute policies that remove barriers to the economically and environmentally sound recovery of metals. Market co-ordination of these actions through either feedback or feedforward control requires multidisciplinary knowledge that link transformations and flows of materials and energy to the dynamics of the metal metabolism. In particular, metallurgical knowledge is essential in this process. In the design of products for environment/recycling, a consideration of the metal grouping in the products, or product components and resulting waste flows is imperative to enable future recovery of metals. The wheel visualizes these interdependencies. For effective (feedforward) control of the system, however, dynamic, predictive/quantitative models of the system are required that are rooted in a solid understanding of technological infrastructure. The (pyro)metallurgists' role is crucial developing such models. They must actively be engaged in making metallurgical knowledge available, and ensure that the databases and models represent the industry. Even if such quantitative models can not completely capture the development and patterns of materials and energy, they may serve as a tool to assist communication between the parties involved and further develop the required multidisciplinary knowledge.

Chapter 5

Electronics Recycling: Lead free solder

In this chapter, an industrial ecology model of the interdependent resource cycles of metals is evaluated as a tool to assist decision-making on complex systems. The lead resource cycle is used as a case study. Lead is a very useful, but also very toxic metal. In the case-study, therefore, two complementary, prescriptive strategies to reduce the environmental and human health impacts associated with the lead resource cycle are examined. First, prevention or detoxification is an important theme in industrial ecology. The EU directive on lead substitution is one of the detoxification strategies. A second strategy is the containment of lead in the industrial system, by process development or increased recycling. This strategy is related to the IE strategies to increase the eco-efficiency, and close the material cycles. Any strategy to reduce the impact of lead requires knowledge of the potential bottlenecks and environmental benefits. This chapter first discusses the toxicity and exposure of lead and the existing legislative framework (Section 5.1). As an example of the first strategy, possible lead substitutes are investigated (Section 5.4) using a comprehensive model of the metal cycles (Section 5.2). As an example of the second strategy, different measures to reduce the emissions from lead use and production are studied (Section 5.5). Finally, some conclusions are drawn with respect to the use of industrial ecology models to support decision-making on these strategies (Sections 5.6 and 5.8).

5.1 Why lead production?

Industrial ecology requires co-ordination across system levels, and between system components. As a consequence, it involves a shift from dealing with relative simple, well-defined subsystems, to dealing with complex and often globally interconnected systems. In the previous two chapters on metal ecology, it was argued that metals that participate in linked cycles can not be analyzed independently, nor can product design, waste management, metals production or legislation/policy be considered separately. In this chapter, a model as a tool to assist decision-making in such complex, interdependent systems is presented and evaluated. Lead production is selected as a case study because on the one hand lead is a very useful metal with a great many different applications, on the other hand lead is a heavy metal with a high toxicity. In this chapter, two complementary strategies to reduce the environmental and human health impacts associated with lead use and production are examined, viz. prevention and containment. Lead emissions can be prevented by substitution of lead in products. This strategy is related to the concept of "detoxification" in industrial ecology. Alternatively, lead can also be "contained" in the industrial system. Increased emission control in industrial and public infrastructures in combination with increased recycling can positively affect the environmental and human health impacts of lead use and production. As a background for these strategies, the sections below discuss the sources of lead exposure (Section 5.1.1), the environmental and human health impacts of lead (Section 5.1.2), and finally the existing legislative framework (Section 5.1.3). A model of the interconnected metal resource cycles is presented (Section 5.2) and evaluated on its potential to support decision-making of the different stakeholders involved using examples of both strategies (Sections 5.4 and 5.5). Finally, conclusions are drawn with respect to the value of the model to co-ordinate decision-making on the design, operation and management of the metal resource cycles (Section 5.8).

5.1.1 Sources

Anthropogenic emissions are the most important source of lead. Natural emissions of lead rarely results in elevated concentrations in any environmental compartment. Lead occurs naturally in low concentrations in all rocks, soils and dusts, usually ranging from 2 to 200 parts per million. In the last two centuries, however, the anthropogenic source of lead has increased dramatically. The total emission to air from natural sources is roughly ten per cent of the total anthropogenic air emissions in the mid-1990s [208]. The ratio anthropogenic/natural emissions for lead is significantly higher than for other heavy metals, such as Hg and Cd, for which anthropogenic and natural emissions are roughly in the same order of magnitude. Anthropogenic sources of lead include release during production, from industrial effluents, dissipative use, disposal and transportation accidents and a wide variety of patterns of use. In 2000, roughly 3.5 million tons of lead were extracted from the earth's crust by man and brought into cycling in the "technosphere" (i.e. the industrial system as opposed to the biosphere). In addition to this, also a significant amount of lead was extracted, but ended up as process residues, or was mobilized as impurity by the extraction of other minerals such as coal and lime. Detailed descriptions of the anthropogenic sources of lead includes the work of Nriagu and Pacyna [209], and more recently Pacyna and Pacyna [210].

Table 5.1: The total world-wide emissions of lead from all sources [209]

	Emission to atmosphere (t/y)	Emission to water (t/y)	Emissions to land (t/y)
Metals and mining industry	31,125 - 83,840	5,560 - 37,320	329,100 - 791, 000
Use and disposal of lead	249,670 - 251,130	4,400 - 2,800	215,800 - 461,700
Other sources	7,886 - 41,854	240 - 1,200	57,190 - 303,700
Total	288,681 - 376,024	10,200 - 66520	602,090 - 1556,400
Atmospheric fall-out		87,000 - 113,000	202,000 - 263,000
Total	288,681 - 376,024	97,200 - 179,520	804,090 - 1819,400

Generally, human exposure to lead comes from the following main sources: Using leaded gasoline, using lead-based paint, having lead pipes in water supply systems, and exposure to industrial sources from processes such as lead mining, smelting, and coal combustion. The major exposure route for the general, non-smoking adult population is from food and water.

Inhalation is the dominant pathway, for workers in industries that produce, refine, use or dispose lead or lead compounds. In countries where leaded gasoline is still used, airborne lead exposure is a significant pathway. Increased awareness and environmental measures may reduce lead emissions as shown for instance by the phase-out of lead in gasoline in developed countries over the last two decades. Von Storch et al. [211] showed how lead emissions in Europe underwent significant changes, from an almost unabated increase to a series of sometimes drastic reductions since the 1970s.

5.1.2 Lead toxicity

The fact that lead is toxic has been known for more than 2,000 years, and its effect on human and environment have been extensively studied [212, 213, 214, 215]. Lead serves no known useful purpose in the human body, and its presence in the body can lead to toxic effects, regardless of exposure pathway. Lead can cause blood-related diseases, is toxic to the reproductive process and suspected to be carcinogenic. Acute high lead exposure can cause serious physiologic effects, including death or long-term damage to brain function and organ systems. Lower levels of exposure have been shown, through population studies, to have many subtle health effects. The effects in children generally occur at lower exposure than in adults [216, 217, 218, 219]. Lead is not degradable in nature. Once released into the environment, it will thus recycle in the physical, chemical and biological processes in the environment. Lead is known to be toxic to plants, animals and micro-organisms. Both wild and domestic animals can ingest lead, for example while grazing, and experience the same kind of effects as people who are exposed to lead. Lead in the environment is typically bound to particles or found as compounds with a relatively low mobility and bioavailability (i.e. the extent to which lead can be assimilated by organisms). Lead accumulates in most organisms, in particular in organisms that primarily feed on particles, such as mussels and worms (a process commonly known as "bio-accumulation"). There appears to be no increase in concentration of the metal in the food chains ("bio-magnification"). Given the increasing evidence of lead toxicity to humans at low levels of lead exposure, its toxicity and persistence in the environment (long-term exposure), it is essential that lead discharges, emissions and losses are prevented, or significantly reduced.

5.1.3 Legislation

In the literature, many overviews of legislation concerning restrictions on lead-containing products in different countries can be found [220, 221, 222, 223, 224, 215]. A number of international agreements have been established in order to manage and control releases of lead to the environment. Perhaps the most well known of these is the Basel Convention that lays down binding commitments regarding the international transport of hazardous waste, and procedures for information and approvals on import and export of hazardous waste. In the convention, any waste containing lead or its compounds as constituents or contaminants is considered a hazardous waste, excluding metal waste in its massive form. In addition, in many countries legislation and standards have developed to contain lead in the technosphere aiming to minimize lead releases to air, water and soil. These include legal standards for maximum concentration of lead in drinking water and quality standards for ambient air, fresh water and salt water, lead threshold limits for occupational air exposure, and emissions limits for the incineration of hazardous and non-hazardous wastes. In several countries, also voluntary agreements between industrial associations and environmental authorities have been used as an alternative to formal legislation. As an example of such an agreement, the European PVC industry has adopted the following reduction targets for replacing lead stabilizers on the basis of 2000 consumption levels: 15% in 2005, 50% in 2010 and 100% in 2015 [220]. In line with the prevention principle, lead substitution has become an increasingly popular approach in Europe to reduce lead emissions at the source. The proposed EU directives on electrical and electronic equipment [225] are exemplary for this approach. Other bans on the use of lead are in place, or are taking effect in the near future, e.g. in vehicles, with certain exemptions [9]. In Denmark already bans on most uses of lead compounds not covered by EU legislation, and on many uses of metallic lead are imposed. The OSPAR Commission recommends that lead should be further substituted where appropriate. However, the commission adds that "a detailed investigation of the use of lead in such products, including the effectiveness and safety of proposed substitutes and an appraisal of the advantages and disadvantages of carrying out specific substitutions will need to be carried out in order to assess the practicability of phasing out lead in products" [220]. As will be illustrated by the case study on lead production, the feasibility and overall environmental benefits of lead substitution or containment are not always obvious.

5.2 Modelling the metal cycles

The problem - and thus the necessity for modelling - for either prevention or containment strategies is that lead processes form an integrated part of the total base-metal production system. Examining the effect of lead substitution, or changes in the lead processes may therefore dynamically affect the production and recycling of many other interconnected metals. To our knowledge, neither in the industrial ecology literature, nor in the metallurgy literature studies have been reported that provide the required in-depth coverage of the dynamics and interconnectivity of the metal resource cycles in technical sense described in the two previous chapters. In this section, therefore, a dynamic model (programmed in Simulink™/Matlab®) is presented which attempts to capture these dynamics. Results of the model simulation are reported for the examples of introducing lead-free solder world-wide, and changes to the technological infrastructure for lead production and recycling. The model presented here is a model, which connects the industrial resource cycles of lead, tin, copper, bismuth, zinc, silver, gold, nickel, and PGMs with each other.

5.2.1 Bottom-up approach

The model has been constructed by employing a bottom-up approach, where the interconnected circuits for metal production are represented by a series of individual processes and/or reactors (see Chapter 3). In Figure 5.1, the model levels are presented. Level II incorporates the five phases in the resource cycle of a metal: Mining, metal production, product manufacturing, consumption, and solid waste management. From level III onward, the levels show increasing technical detail. Level III shows the interconnected metal production circuits (see also Figure 3.13). In level IV, the different production routes for a single metal are shown. Level V zooms in the model of each process step. This hierarchical method of modelling and representation provides a transparent overview of the interconnected metallurgical production circuits. This transparent view is well suited to initiate further development of the products or the production network by the stakeholders at different system levels; for example by making changes in the metallurgical production networks visible to waste managers, policy-makers, legislators, or product designers.

Mass-balance calculations based on data reconciliation allow simulation of system change and track the effect on the system performance. In addition, the model is structured in such

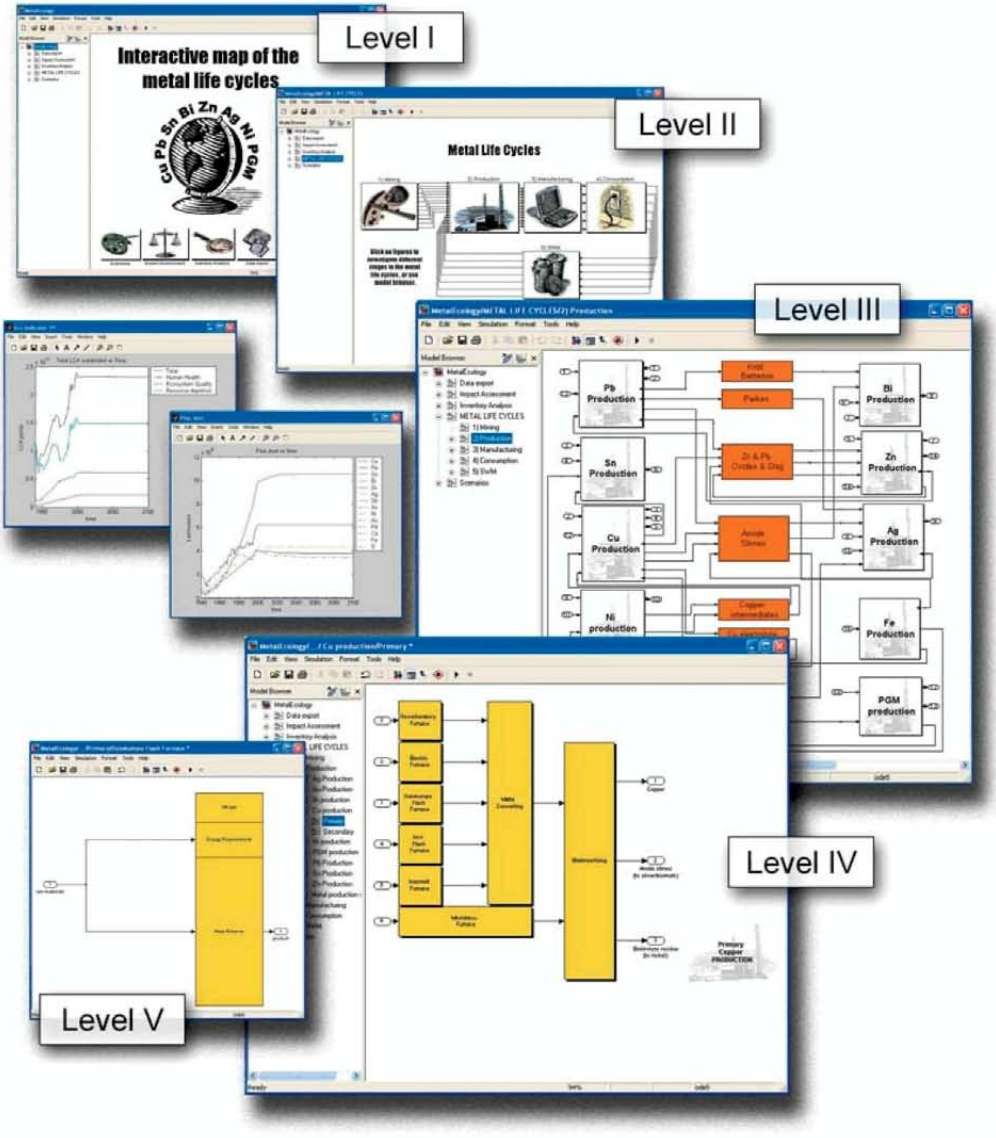


Figure 5.1: Interconnected metal cycles in Simulink™(Matlab®)

a way that emissions can be traced down to individual processes or reactors. The model allows the investigation of a wide range of scenarios, because all parameters can either be fixed over time or given a scenario for change over time. The effect of the development of new products can be modelled by a change in the metal production rates, distribution of the metals concerned over products and waste categories. A new technology or process step can easily be included in the model because of the bottom up modelling approach combined with the modular structure of Simulink™/Matlab™programming environment. By using the options available for parameter manipulation, the effects of a shift in employed technology can be analyzed.

5.2.2 Flowcharts of the metal cycles

In order to adequately and realistically capture the dynamics, any model of a metals production infrastructure or part thereof, must have sufficient scope to account for the interconnectedness and interdependencies in the global system, as discussed in Chapter 3 and summarized in the metal wheel. For the case study on lead production, at least the interconnected zinc, copper, tin, silver, and bismuth cycles must be modelled. In the model, the flows between the production processes consist of these metals, but also of representative co-elements (impurities in the wheel): antimony, arsenic, nickel, gold, platinum, palladium, rhodium, cadmium, cobalt, iron and sulphur. The elements considered allow a good representation of the compositions of the residues, leachates and emissions. Such modelling has to be based on the fundamental thermodynamics of each metallurgical reactor, its geographical distribution and the prevalent knowledge (see Chapter 3). To meet these criteria, literature reports of the individual process steps in the production of metals were reviewed to obtain input and output data for each process step in the network. An integrated flowchart of primary zinc and lead production was given in Chapter 3, detailed production/recycling flowcharts for all metals are given in Appendix B. In the dynamic modelling of these flow charts, two types of parameters determine material flows as a function of time: Process and structural parameters (Figure 5.2). The process parameters ($p_{j,i}$) determine which part of the raw material is converted to one of the four possible outputs: Product, intermediate, residue or emission in process step j. Because the thermodynamics and physics of the processes are not always fully understood, and process outputs are partially controlled with the tacit knowledge of the process personnel, these parameters are difficult to determine and can vary between different processes, or with feed composition. Consistent with the research of Reuter [23], linear relationships between feed and process outputs were used to approximate the fundamental thermodynamics and physics in each production and process step. Each process can produce five different products: Product 1 ($i = 1$) of a process j as function of time is given by process parameter, $p_{j,1}$, multiplied by its the feed. Data reconciliation was used to resolve discrepancy between data, which was often collected for different purposes, and to obtain reliable process parameters. In addition, extensive industrial knowledge obtained through reliable personal industry contacts, as well as extensive in-house knowledge ensured that the data is of high quality and reflects the current state-of-the-art. The structural parameters (s_n) determine the flow of material through the different processing routes and thus the feed of the different processes. At any point in time, the feed of process 1 is given by multiplication of the supply of raw material at that time by the structural parameter s_1. Distribution of the mass flows over the process routes is based on the literature and extensive experience. The partitioning of the elements over the mass flows is determined by dividing the average (reconciled) feed compositions by the total composition of raw materials. Note that for primary material, new scrap and old scrap routes, the structural parameters differ. In the flowchart, two processes (process 1 and

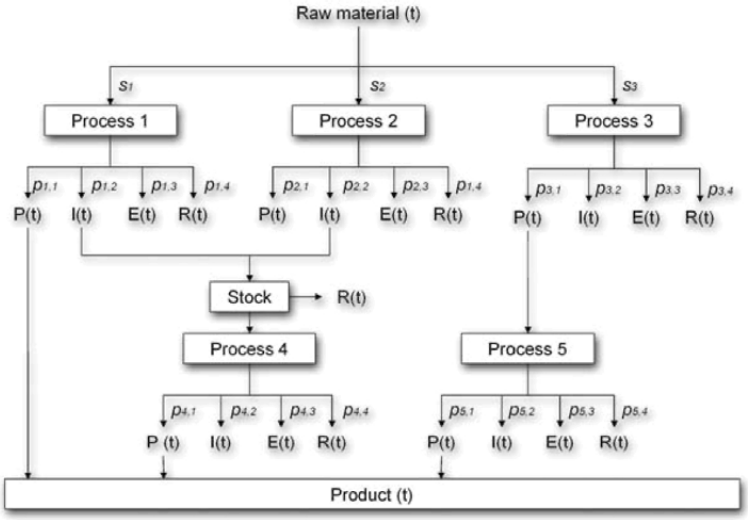


Figure 5.2: An example of a flowchart for the production of a metal consisting of five different processes; Legends: P = product, I= intermediate, E= emissions, R= residue, $P_{j,i}$ = process parameter, and S_j = structural parameter

2) produce an intermediate that is consumed by another process (process 4). The other two processes produce intermediates, but these are not used and disposed of. The amount of intermediate disposed of ($R(t)$ from the intermediate stock in Figure 5.2) is determined by the average residence time of the intermediate in the stock (1 year), the demand for (process 4), and supply of intermediate (processes 1 and 2).

Global mining and metal production figures were obtained from metal statistics [226, 227]. The return flows to production from recycling were based on worldwide statistics reported on the fraction of metals recovered from secondary sources [228, 226, 229, 146, 227, 230]. Depending on the end uses of the metal, different life spans were assumed in the modelling of the distributed nature of the consumption phase. Per metal, the mass balance was completed by assuming that materials were either recycled or disposed of on landfills, or incinerated.

5.3 Detailed Model description

This section gives a detailed description of the model. The code of the model is added as a CD (see Appendix D), making all the data available for general use.

5.3.1 General model framework

Substance Flow Accounting (SFA) is used as basis for the model. SFA models belong to the family of Material Flow Accounting (MFA) models, with which the physical aspects of human activities can be mapped [231, 232]. As discussed in Chapter 2, a MFA model is based on the principle of mass preservation and describes flows, accumulations of materials in the economy and the environment. As there is no standardized framework for SFA, as there is for LCA, the LCA framework is used. The Leiden University Centre for Environmental Science adopted and modified the LCA framework for SFA [233, 41, 117, 234]. This framework consists of three distinct phases, which structure the analysis, and are based on the technical framework of LCA:

- *Objective and system definition*: This first phase corresponds to the first phase in LCA, Goal and scope, and involves four choices. The first step SFA modelling is the choice of the objective of the study. According to the goal of the study, the second step is to establish whether the studied system should correspond to a certain region, the regional approach, or a certain function, the functional approach. This also involves the definition of subsystems. The third step is the time span. Often, in MFA studies a one year period is chosen, and the accumulated flows for the region or the function are determined for that period. The fourth step concerns the materials and flows to be studied. A SFA can be carried out for a single substance, or a number of related materials (e.g. connected to a function).
- *Inventory and modelling*: This phase correspond to the second phase in LCA, the inventory phase and involves identifying, collecting and organizing relevant data. This data can be organized in one of three different types of modelling, all three types having there own data requirements, viz. bookkeeping, static modelling and dynamic modelling.
- *Interpretation*: The last stage of an MFA study is to interpret the quantitative results on flows and stocks. For an MFA study where only one substance or group of substances is studied, the interpretations of the result might be relatively simple. This is not the case for complex MFA studies with several materials. In these studies, the result may be interpreted by using environmental issues, or environmental impact categories, such as global warming, eutrophication, or acidification [117]. This is the same procedure as in LCA, where it is called classification and characterization. Thus, this phase corresponds roughly to phase 3-6 in LCA: Choice of impact categories, classification, characterization and weighting, although the latter is not always performed.

In the following sections, the general layout of the model is discussed based on these three phases.

Goal and system definition

An SFA can be used for quite different purposes: as a support for data acquisition, for the analysis of trends and their causes, for the identification and the prediction of the effectiveness of environmental measures, and as a screening tool, identifying issues for further investigation by other tools [117]. In the identification or evaluation of potential policy measures SFA offers the possibility to predict the emergence of new or unexpected problems. In the SFA model developed, the objective is to investigate the consequences of policy measures, viz. replacing lead in solder for electronic and electrical appliances on the global metal cycles. The specific focus of the study is on the effects on the production and recovery of metals. Often an SFA deals with one substance only. If measures are taken to reduce the use of the substance under study by replacing it by another substance, problems connected with this other substance are outside the scope of such studies. Rather than s single substance the model therefore deals with a group of metals that are related to the production of lead (free) solder, as well as a representative selection of the co-elements associated with those metals. The metals investigated in this study are copper, lead, tin, bismuth, zinc, nickel, silver, gold and three platinum group metals (PGMs: platinum, palladium and rhodium). In addition, the following co-elements are considered: sulphur, arsenic, antimony, cadmium, iron, and cobalt. In the determination of emissions of the different processes involved in the production and recovery of the metals, also nitrogen, oxygen and carbon are included. The selection of elements allows a good representation of the compositions of the material flows through the system. The choice of the materials investigated sets the system boundaries of the modelled system. The market for metal production is global; the concentrate, scrap, metal and valuable intermediates are transported and traded worldwide. Consequently, metals are produced by an entangled network of interconnected production routes, rather than by geographically isolated production centers. The system boundaries of the SFA are function based; the focus of the analysis is the global metal production system. The time span of the study is determined by the dynamics of the global metal production system. The study focuses on the global lead production system, and investigates the effects of the introduction of a number of lead-free solders in the present global metal production system. Because of the delays in the system, it takes time before the substitution of lead in solder has trickled through the global system, and the effects can be evaluated. The time span of the study is therefore at least the life span of electrical and electronic appliances in which the lead is substituted. Moreover, to estimate the waste flows returning to the metal production system (and partially replacing the virgin ore concentrates) the historical metal production must be integrated over a maximum of roughly 60 years, obviously dependent on assumptions for the average life spans of the different metals considered. With respect to the definition of subsystems, it is usual to make a distinction between the "society" and the natural environment. Within society, the attention is generally focused on the physical economy. SFAs and MFAs refer to accounts in physical units comprising the extraction, production, transformation, consumption, recycling, and disposal of materials (e.g. ores, raw materials, base materials, products, wastes, and emissions). In the model, therefore, the physical economy is further divided into mining, metal production, product manufacture, consumption and solid waste management compartments. The environment is often split into a number of environmental media such as lithosphere (i.e. the earth's crust), atmosphere, hydrosphere, soil (or pedosphere) and biosphere. Metal production processes directly affect the atmosphere, soil and part of the hydrosphere (mainly groundwater), which in turn influence the other parts of the hydrosphere and the biosphere. In the model the environment is split into only these first four compartments, the induced changes are considered in the interpretation phase. Note that in contrast to LCA, the definition of the borderline between society and environment in SFA is not so much a critical issue. The core issue in LCA concerns the transgression of substances over this borderline, either as the extraction of resources or as the emission of hazardous substances. SFAs consider both the accumulations within the environment and the economy; therefore, the possible effects are considered, independent from the precise definition of the borderline between the two subsystems [41].

Inventory and modelling

This step involves identifying, collecting and organizing relevant data. De Haes and Van der Voet [41] distinguish at least three types of models for the modelling of flows and stocks: (i) book keeping, (ii) stationary modelling and (iii) dynamic modelling. Considering the interdependent dynamics of the metal production systems, the dynamic model seems the logical choice for the SFA model developed. The modelling approach and the modelling of the five stages that together represent the life cycles of a metal will be discussed in more detail in Sections 5.3.2-5.3.3.

Interpretation

The last stage of an MFA study is to interpret the quantitative results on flows and stocks. In most SFA studies, the output is defined in terms of flows and accumulations of the material under study. The relevance of the analysis is generally directly related to the hazardous character of the chosen material and will need no further specification [117]. In some cases, there is an explicit need for further elaboration of the SFA results, for example, if a group of substances is studied. Here it is difficult to make a comprehensive interpretation of such an amount of data without some form of aggregation. A possible way to interpret the outcome of SFA studies is the specification of the contributions of the substances to a number of environmental issues or environmental impact categories, such as global warming, ozone depletion, and acidification. This approach links up with the development of LCA impact assessment methodology. An example of such approach is the recent SFA study on chlorinated hydrocarbons in The Netherlands (Kleijn et al. in: Udo de Haes et al. 1997) [41] that used environmental impact categories such as global warming, ozone depletion and ecotoxicity. Other examples include the studies on chlorine and PVC for the Dutch government and Norsk Hydro that also combined elements of SFA and Life Cycle Impact Assessment (LCIA) [115, 112, 113]. Based on the studies Tukker and Klein [114] conclude that environmental evaluation methods like SFA and LCA can successfully be used in combination. Obviously, the output of an SFA of the complex, global interconnected metals cycles requires aggregation in some way to enable interpretation. The SFA model is therefore combined with elements of LCIA. This is discussed in more detail in Section 5.3.4.

5.3.2 The inventory and modelling approach

The focus is on the operation of the interconnected metal cycles, more specifically on the production and recovery of metals. In order to properly assess the environmental aspects of metallurgy, or to adequately capture the interdependent dynamics of the global system, modelling is required that is based on the fundamental thermodynamics in each metallurgical reactor, of waste processing step. For that reason, the dynamic inventory has been constructed by employing a bottom-up approach, where the interconnected circuits for metal production and recovery are represented by a series of individual processes and/or reactors. The SFA inventory is modelled in Simulink™, an interactive graphical interface for modelling, simulating and analyzing dynamic systems in Matlab®(Mathworks Inc. [235]™). The equations that constitute the dynamic system model are input by the selection and connection of the appropriate blocks that represent elementary mathematical operators. In the dynamic simulation, Simulink™calculates all blocks in a given order for each time step.

The first level in Figure 5.1 shows the general menu to access the mass balances, impacts assessment, dynamic inventory or different scenarios. The second level incorporates the five phases in the life cycle of a metal: mining, metal production, product manufacturing, consumption, and waste management. The third level shows the interconnected metal production systems. The higher levels show increasing technical detail: the different process steps in the production of these metals, and interconnections between the metal production processes in more detail. At all levels of detail, a description of the flowsheets and flowsheet components is given, which can be accessed by clicking on the info button (general information) or on each of the different flowsheet components. As mentioned in chapter five, this hierarchical method of modelling and representation provides a transparent overview of the interconnected metallurgical production circuits, and would be suited to initiate further development of the products, or the production network by the stakeholders involved. As such, the model could assist in making the complex metallurgical knowledge available for waste management, policy and product design. Mass-balance calculations based on data reconciliation allow simulation of system change and track the effect on the system performance. In addition, the model is structured such that emissions can be traced down to individual processes or reactors. The modelling approach allows the investigation of a wide range of scenarios, because all parameters can either be fixed over time or given a scenario for change over time. For instance, the effect of the development of new products can be modelled by a change in the metal production rates, distribution of the metals concerned over products and waste categories. Alternatively, a new technology or process step can easily be included in the model because of the bottom up modelling approach combined with the modular structure of Simulink™, the Matlab®programming environment. By using the options available for parameter manipulation, the effects of a shift in employed technology can be analyzed.

Modelling of the metal life cycles

As discussed in Chapter 3, the environmental impact and efficiency of metal production is dependent on the total demand for the metal, but also on the demand for other metals via intermediates, and the availability of other metal resources, viz. new and old scrap. In particular secondary materials are increasingly important raw materials for the production of metals. The rate of generation of the secondary raw materials and their compositions, are a function of the combination of metals and other materials into different products, and the lifespan of these products (see Chapters 3 and 5). Level two of the model (Figure 5.3) shows this interdependence between the different stages in the metal life cycle. An important aspect of the Simulink™model developed is that it allows dynamic simulations of the operation of the interconnected metal cycles, in particular the changing interdependencies in the production and recovery of metals. Until recently, quantitative descriptions of the physical economics have concentrated mostly on flows without considering the build-up of stocks in the economics [147]. During the past few years, researchers have realized that the delay of materials in the consumption phase is an essential component of such descriptions, for example in the prediction of future emissions and waste flows [162, 236, 147, 237, 238]. Today's stocks are tomorrow's emissions and waste flows. Moreover, because of the time lag introduced by the buffering function of the stock of materials and products in society flows, which seem to be under control, can easily rebound. Large stocks of metals have accumulated in the economic system, which must be dealt with in some way or the other. An increasing fraction of secondary raw materials in metal production may significantly reduce the grade of the produced metals (see Chapter 4). To develop an adequate waste and metallurgical infrastructure to recycle the wasted metals into high-grade raw materials, information on the amount of wastes, and material combinations flowing from the economic stocks is required. Figure 5.3 shows the different stages of dynamic mass balance of the interconnected metal life cycles, which form the basis of the model.

Mining

The efficiency and environmental impact of metal mining and extraction is not constant but is a function of the mining and extraction route. The mining and extraction route for each ore is modelled separately. The demand for ore is dependent on the total demand for a metal and the availability of other metal resources, viz. new and old scrap, intermediates. Based on the emissions, energy consumption and recovery of each mining and concentration route, the emissions to air, water and soil, and the production of the different ore concentrates are calculated as a function of time as defined by Eq. 5.1.

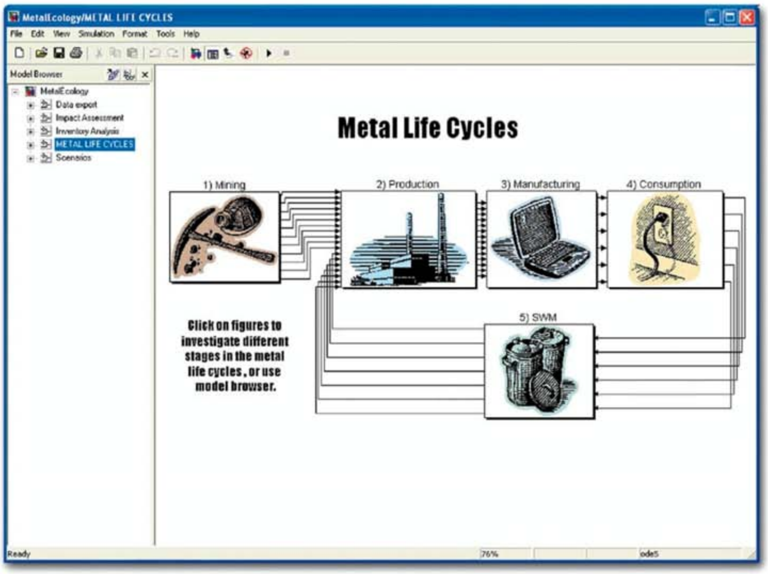


Figure 5.3: Level two of the Simulink™model shows the different stages in the metal life cycle

$$\begin{aligned} D_{ore}(t) &= \left(f_{air}(t) + \sum_{i=1}^{i=m} f_{orec,i}(t) \right) \cdot D_{ore}(t) + \sum_{n=1}^{n=2} L_{n,t}(t) \\ &+ \frac{d(LF_{stock,t}(t))}{dt} \end{aligned} \tag{5.1}$$

where:

$D_{ore}(t)$ = Demand for ore (ton/a)
$f_{air}(t)$ = Fraction of ore emitted into air (ton/ton)
$f_{orec,i}(t)$ = Fraction of ore processed into ore concentrate i (ton/ton)
m = Number of ore concentrates i produced
n = Environmental compartments water and soil
$L_n(t)$ = Leachate from disposed tailings into environmental compartment n (ton/a)
$LF_{stock,t}(t)$ = Stock of tailings disposed (ton)

Metal production

The metal production phase is modelled bottom up starting from individual process steps. The different metal production flowcharts presented in Appendix B were modelled as described in Sections 5.3.3 to 5.3.3. Dependent on the availability of metals resources (new and old scrap, intermediates and ore) the metals are produced through the different processing routes as defined by Eqs. 5.2 and 5.3.

$$P_j(t) = \sum_{i=1}^{i=r} \sum_{n=1}^{n=m} f_n(t) \cdot R'_{j,i}(t) \tag{5.2}$$

$$R_j(t) = D_{ore,j}(t) + NS_j(t) + S_{i.m.,j}(t) + S_{sec,j}(t) \tag{5.3}$$

where:

$P_j(t)$ = Production of metal j (ton/a)
f_n = Fraction of waste j processed through route n (ton/ton)
$R_{j,i}$ = Supply of metal resource i for the production of metal j (ton/a)
NS_j = Supply of new scrap of metal j (ton/a)
n = Metal production route
r = Number of different metal resources
m = Number of different metal production routes

Based on the emissions, energy consumption and recovery of each route, the emissions to air, water and soil, and the production of the different metals are calculated as a function of time as defined by Eq. 5.4.

$$R_j(t) = \left(f_{air}(t) + \sum_{i=1}^{i=m} f_{pr,i}(t) \right) \cdot R_j(t) + \sum_{n=1}^{n=2} L_{n,pr}(t) + \frac{d(LF_{stock,pr}(t))}{dt} \tag{5.4}$$

where:

$f_{p,i}$ = Fraction of resource j processed into intermediate or metal i (ton/a)
$L_{n,pr}(t)$ = Leachate from disposed process residues into environmental compartment n (ton/a)
$LF_{stock,pr}(t)$ = Stock of disposed process residues (ton)
m = Number of different metals and intermediates produced

Note that the different production routes for the metals are not constrained by a maximum capacity; an increase in the production volumes of the metals does not affect fraction of metal produced through a production route. Because of the modular structure these constraint can easily be added.

Manufacture and consumption

To estimate composition and quantity of the generated waste at a point in time, or the dynamics in the metal cycles in case of disturbance, the delays in the consumption (life spans of the products) need to be estimated. In the model the delays in the production of metals are assumed negligible compared to delays in the consumption phase, that vary from less than one year to well over fifty years. The metals are manufactured into five hypothetical products to estimate the average delays of the metal in the consumption phase. Energy consumption and emissions to air and manufacturing residues other than new scrap, or the energy consumption during consumption are not included in the model. Eqs. 5.5 and 5.6 describe the manufacturing and consumption phase respectively.

$$P_j(t) = \sum_{i=1}^{i=n} NS_{j,i}(t) + \mathrm{Pr}_j(t) \tag{5.5}$$

$$\begin{aligned} \mathrm{Pr}_j(t) &= \sum_{j=1}^{j=m} W_j'(t) + \sum_{n=1}^{n=2} L_{n,du,j}(t) + \frac{d(LF_{stock,du,j}(t))}{dt} \\ &+ \frac{d(LF_{stock,pro,j}(t))}{dt} \end{aligned} \tag{5.6}$$

where:

$NS_{j,i}(t)$ = generation of new scrap of metal i in the manufacture of product j (ton/a)
$P_i(t)$ = production of metal i (ton/a)
f_i = fraction new scrap of metal i (ton/ton)
n = Environmental compartments water and soil
$L_{n,du,j}(t)$ = Leachate due to dissipative use of product j into environmental compartment n (ton/a)
$LF_{stock,du,j}(t)$ = Stock of product j that is used dissipatively (ton)
$LF_{stock,pro,j}(t)$ = Stock of product j that is not used dissipatively (ton)

The modelling of new scrap generation, the composition of the products, the accumulation in consumption phase and the emissions from dissipative use of metals are discussed in the next sections.

Solid waste management

The solid waste management phase is modelled in a similar way as the metal production phase. The different solid waste management routes as presented in Appendix B were modelled as described in Sections 5.3.3 and 5.3.3. As a function of the final products of metals and other substances collected as waste j waste is disposed and recovered through the different processing routes as defined by Eq. 5.7.

$$W'_j(t) = \sum_{n=1}^{n=m} f_n(t) \cdot W'_j(t) \tag{5.7}$$

where:

f_n = Fraction of waste j processed through route n (ton/ton)
n = MSW, WEEE, ELV, C&D and other recovery
m = number of different waste processing routes

Based on the emissions, energy consumption and recovery of each route, the emissions to air, water and soil, the composition and quantity of the recovered metal concentrates and the accumulation in the solid waste management system is calculated as a function of time (Eq. 5.8).

$$W'_j(t) = \left(f_{air}(t) + \sum_{i=1}^{i=m} f_{conc.i}(t) \right) \cdot W'_j(t) + \sum_{n=1}^{n=2} L_n(t) + \frac{d(LF_{stock}(t))}{dt} \tag{5.8}$$

where:

$f_{air}(t)$ = Fraction of W'_j emitted into the air (ton/ton)
$f_{conc.i}(t)$ = Fraction of W'_j recovered as concentrate i (ton/ton)
n = Environmental compartments, soil and water
m = Number of different metal concentrates
$LF_{stock}(t)$ = Stock of metals and substances disposed of on landfills (ton)

The energy consumption is mainly a function of the energy required for the transport of the waste in the collection, processing and delivery to the metal production facilities.

5.3.3 Bottom-up approach

In the next section, the bottom up modelling approach used to model metal production and recycling is further elaborated starting from the modelling of individual processes to the interconnected metal production and recovery flowcharts. Subsequently, the modelling of the mining, consumption, and manufacturing stages is discussed.

Level V: Individual processes

Figure 5.4 shows a process model in Simulink™, consisting of mass balance, energy and emission (Off gas) calculations blocks. The calculations in these three blocks are discussed in the sections below.

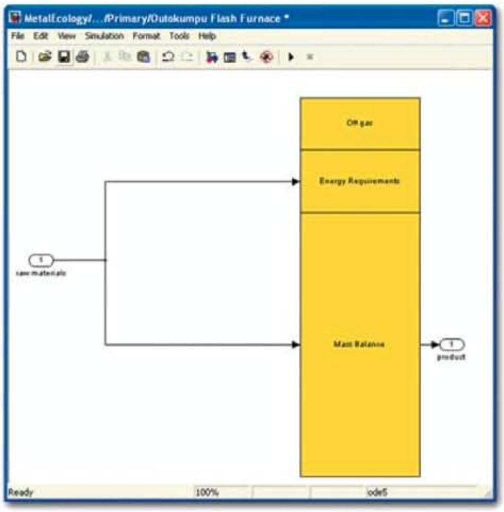


Figure 5.4: An individual process in Simulink™

The mass balance of a process The core of both the stationary and dynamic model is the development of a consistent mathematical structure, which renders it possible to specify relations between the different flows and stocks within the system. In this way, specific problem flows can be analyzed with regard to their origins. In addition as argued above, for an assessment the environmental aspects of metallurgy, or the modelling of the impact of a system change on the pattern and the balance of relationships between processes, dynamic modelling of the total system is required. Such modelling has to be based on the fundamental thermodynamics of each metallurgical reactor, its geographical distribution and the prevalent knowledge. To meet these criteria, literature reports of the individual process steps in the production of metals were reviewed to obtain input and output data for each process step in the network (in the mining, metal production and solid waste management stages). This is consistent with the preferred use of data regarding the distribution characteristics of the processes themselves. After Reuter [23] linear relationships (split-factors) between feed and process outputs were used to approximate the fundamental thermodynamics in each production step.

The process split-factors (the vector of distribution fractions of the feed over the product, by-product, emission and residue streams respectively) are calculated by mass balancing the total mass flows in and out the process (Eq. 5.9), as well as the mass flows of 14-17 chemical elements individually, dependent of the processes considered (Eq. 5.10). Elements considered were copper, lead, tin, bismuth, zinc, silver, antimony, arsenic, nickel, gold, palladium, cadmium, iron, sulphur, cobalt, platinum and rhodium. In such a way dependent on feed quantity, amounts and compositions of products, by-products and residues can be calculated as a function of time. Mathematically Figure 5.5 can be defeind by Eq. 5.10.

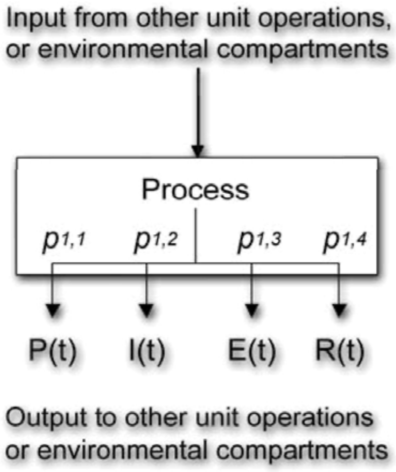


Figure 5.5: Schematic representation of a unit operation model

$$\varphi_{in} = \sum_{i=1}^{n} \varphi_{out,i} \tag{5.9}$$

$$\varphi_{in,j} = \sum_{i=1}^{n} \varphi_{in,j} \cdot p_{i,j} \tag{5.10}$$

where:

j	denotes the vector elements: mass flow (Q), Cu, Pb, Sn, Bi, Zn, Ag, Sb, As, Ni, Au, Pd, Cd, Fe, S (Co, Rh, Pt).
i	denotes output stream: product P, intermediate I, emission E or residue R.
φ_{in}	denotes the process feed,
$\varphi_{out,i}$	denotes the output stream i,
$\varphi_{in,j}$	denotes element j in the process feed vector,
$\varphi_{out,i}$	denotes element j in the output stream i vector, and
p_i	denotes element j in split factor for output stream i.

A problem of the modelling approach adopted is that detailed information on the compositions of products, by-products and waste is needed to calculate split factors for each process in the network. These compositions could be obtained from literature reports on different plants, however, data was often not consistent and mass balances could often not be closed. This is a common problem in engineering, where mass balances based on measured data often are not complete. This is usually caused by inaccuracy of the measurements because of the sampling, measurement and analysis errors as well as the very lack-of-measurements. Madron

[148] and later Veverka and Madron [149] gave overviews of data reconciliation: a set of methods used to adjust the experimental data to reduce and possibly eliminate discrepancies in the mass balance. Data reconciliation is basically minimizing a sum of errors (the difference between each measured data and its reconciled value) weighted by the standard deviation of the measurement, subject to a number of constraints (the mass balance equations). The mathematical denotation for the data reconciliation are given by Eqs. 3.1 to 3.5.

Adjustments to experimental data are subjected to a number of restrictions, viz. the conservation of global flow rate (Eq. 3.3), the conservation of global and elements flow rates (Eq. 3.4) and the data integrity constraint (Eq. 3.5).

In the reconciliation of the mass balances of processes for the dynamic modelling, the data is not based on measurements, but on processing data of plants around the world found in the literature. The essentials of the data reconciliation technique, however, remain the same. Calculation of the average compositions as a basis for constructing the mass balance normally does not result in a completed mass balance of the unit operation employing linear algebra. Using the standard deviation in the data as a measure for the accuracy of the data, a closed mass balance can be obtained using data reconciliation. Because the thermodynamics and physics of the processes are not always fully understood, and process outputs are partially controlled with the tacit knowledge of the process crew, these split-factors are difficult to determine and can vary between different processes, or with feed composition. The work of Reuter [23] showed that the approach taken provides for a good representation for average process operation. The software used for data reconciliation is Excel 2000. The maximum number of elements that can be reconciled is limited by the computational capacity of Excel's standard solver, and therefore only critical elements were included in the mass balance. Further details of the reconciliation process and the raw data can be found in Scholte [150] and Van Tweel [151].

The emissions of a process Based on the mass balance emissions, material and energy consumption of the process are calculated (Eq. 5.12). Solid wastes are not considered emissions, however their subsequent disposal on landfills does lead to the leaching the metals, which results in environmental hazards to soil and groundwater (see Impact assessment 5.3.4). One percent of the flue dusts was assumed to leave the process together with the off gas. The bulk (90%) of the captured flue dust is recycled internally or externally (e.g. in zinc plants) and the remainder is disposed off on landfills. Gaseous emissions are calculated based on the mass balance and the addition of reagents. SO_2 is produced from oxidizing metal sulphides; SO_2 production from fuels is neglected.

$$SO_2' = Q_{S,offgas} \cdot X_{S,ton/mol} \tag{5.11}$$

$$SO_2 = SO_2' \cdot \frac{M_{SO_2}}{\rho_{SO_2}} \tag{5.12}$$

where:

$Q_{s,offgas}$ = Tonnes of sulphur in the off-gas (t)
$X_{S,ton/mol}$ = Conversion factor tonnes sulphur to moles of sulphur
M_{SO_2} = Molar mass SO_2 (kg/mol)
ρ_{SO_2} = Density of SO_2 (kg/m^3)
SO_2' = Moles of SO_2 produced (mol)
SO_2 = Cubic meters of SO_2 produced (m^3)

The bulk of the sulphur in the feed reports to the off gas: In the process sulphur in the feed is oxidized to sulphur dioxide. The produced sulphur dioxide is then converted to sulphuric acid in a sulphuric acid plant. Based on literature survey [151] it is assumed that 99% of the SO_2 produced is captured and converted to H_2SO_4 with an efficiency of 97.49%. The coke and oxygen required in pyrometallurgical reduction processes leave the furnace together with the off gas as carbon dioxide. The amount of carbon dioxide was calculated using literature values carbon feed (as cokes) and simple chemistry: Cokes are added for two reasons: (i) as a fuel; in the presence of oxygen part of the carbon in the cokes is oxidized to carbon dioxide, which is an exothermic reaction generating energy, and (ii) as a source for carbon monoxide, the reducing agent to convert metal oxides into their metallic from. The carbon monoxide is produced by the reaction of the solid carbon particles to carbon monoxide, or by partial reduction of carbon dioxide. Reduction of the metal oxide produces carbon dioxide (Eq. 5.13). The remaining carbon monoxide in the off gas is mostly oxidized to carbon dioxide both restrain carbon monoxide emissions and to recover energy. Although in practice efficiency will be lower than 100%, a full conversion was assumed.

$$CO_{2,total} = CO_{2,process} + CO_{2,fuel} + CO_{2,transport} \tag{5.13}$$

where:

$CO_{2,total}$ = total CO_2 production (m^3)
$CO_{2,process}$ = CO_2 production due to the reduction of metals (m^3)
$CO_{2,fuel}$ = CO_2 production due to burning fuels during processes (m^3)

Metal oxides are usually reduced to metals using carbon; the amount of CO and CO_2 created during this reduction process is calculated by Eqs. 5.14 to 5.17.

$$CO_p = Q_{in} \cdot X_{carbon} * \frac{10^6}{M_C} \tag{5.14}$$

$$CO_2' = \sum_{14}^{2} Q_{i,p} \cdot X_{i,ton/mol} \cdot X_{oxides/metal_i} \tag{5.15}$$

$$CO_{2,process} = CO_2' \cdot \frac{M_{CO_2}}{\rho_{CO_2}} \tag{5.16}$$

$$CO = (CO_p - CO_2') \cdot \frac{M_{CO}}{\rho_{CO}} \tag{5.17}$$

where:

CO_p = theoretical CO production (mol)
Q_{in} = total input quantity (t)
X_{carbon} = carbon input as a percentage of the total input
M_C = mol mass of carbon (kg/mol)
CO_2' = mol CO_2 produced (mol)
$Q_{i,p}$ = tonnes of produced metali (t)
$X_{i,ton/mol}$ = conversion factor converted tonnes to moles for metalioxide
$X_{oxides/metal_i}$ = moles of O needed to oxidize one mole of metali
M_{CO_2} = mol mass of CO_2 (kg/mol)
ρ_{CO_2} = density of CO_2 (m^3/kg)
CO = actual CO production (mol)

M_{CO} = mol mass of CO (kg/mol)
ρ_{CO} = density of CO (m^3/kg)

Oil, gas and coal burned for energy during the process also generates CO_2 dependent on the carbon content of the fuels (Table 5.2). The type of liquid fuel used in processes can be any of the four in Table 5.2, an average for oil was taken ($X_{CO_2,oil} = 2.83$). It is assumed that no CO is produced, only CO_2 (Eq. 5.18).

$$CO_{2,fuel} = \sum_{f=1}^{i=f} X_{CO_2,i} \cdot Q_i \tag{5.18}$$

where:

$CO_{2,fuel}$ = CO_2 produced through burning fuel (kg)
$X_{CO_2,i}$ = CO_2 produced per quantity of fuel burned (kg/kg)
Q_i = Quantity of fuel i used (kg)

Table 5.2: CO_2 production for different types of fuels

Fuel type	CO_2 emission
Gasoline	2.39 kg/l
Diesel	2.67 kg/l
Light fuel oil	3.128 kg/l
Heavy fuel oil	3.129 kg/l
Natural gas	1.77 kg/m^3
Coal	2.73 kg/kg

The NO_x emissions of a process are determined by the formation and capture of the NO_x (Eq. 5.19).

$$E_{NO_x}(t) = C_{NO_x} \cdot \sum_{i=1}^{i=n} F_{NO_x,i}(t) \tag{5.19}$$

where:

$E_{NO_x}(t)$ = Emmisions of NO_x (ton/a)
C_{NO_x} = Capture efficiency NO_x (ton/ton)
$F_{NO_x,i}$ = NO_x formation through mechanism i (ton/a)
n = Number NO_x of formation mechanisms

There are three different formation mechanisms for NO_x:

- *Thermal formation* from N_2 in the air,
- *Prompt for NO_x formation*, which converts N_2 into NO in the flame front, and
- *Fuel for NO_x formation*, in which the nitrogen in the fuel is oxidised to for NO_x.

Thermal formation typically starts at 1300°C depending on the oxygen concentration. The amount of excess oxygen depends on the process. A distinction is made between reductive or oxidative processes, where the latter obviously have higher excess of oxygen than the former. Thermal NO_x formation can be estimated by Eqs. 5.20 and 5.21.

$$N_2 = (CO_p + SO_2) \cdot \frac{M_{O_2}}{\rho_{O_2}} \cdot \frac{C_{Air,N_2}}{C_{Air,O_2}} \tag{5.20}$$

$$F_{NO_x,thermal}(t) = N_2 \cdot \left(1 - O_{2,excess}^{-1}\right) \cdot \frac{C_{Air,N_2}}{C_{Air,O_2}} \cdot 100 \tag{5.21}$$

where:

C_{Air,O_2} = Oxygen concentration in the air
C_{Air,N_2} = Nitrogen concentration in the air
$O_{2,excess}$ = Excess oxygen during the process
Reductive processes $O_{2,excess} = 1.025$,
Oxidative processes $O_{2,excess} = 1.1$

Prompt NO_x formation is negligible ($F_{NO_x,prompt}(t) \approx 0$). The fuel NO_x formation depends on the nitrogen content of the fuel used and the combustion method used. It is assumed that 50% of the nitrogen in the fuel is oxidized to NO_x (Eq. 5.22).

$$F_{NO_x,fuel}(t) = 0.5 \cdot \sum_{i=1}^{i=f} F_i(t) \cdot C_i \tag{5.22}$$

where:

$F_i(t)$ = Consumption of fuel i
C_i = N_2 concentration of fuel i
n = Number of fuels

Finally, NO_x emissions are reduced by selective catalytic reduction, in which NO_x is reduced to N_2. The efficiency of this reaction ranges from 60% to 90%. An average capture of NO_x (C_{NO_x}) of 75% is assumed.

Oxygen demand for the different reduction and oxidation reactions were obtained by the construction of phase diagrams (1000°C) of the metals in an environment of sulphur and oxygen. Because furnaces are generally working at atmospheric pressure, only metal oxides and sulphides likely to occur at the lowest sulphur dioxide and oxygen pressures were included in the calculations. In the calculations of the oxygen demand, the oxygen consumed oxidation of the nitrogen was not considered. It was assumed that oxygen is not present in the off gases (oxygen is assumed not be added in excess). Although in reality this is not the case, the assumption does not affect the environmental score of the processes.

The energy consumption of a process Metal production requires considerable amounts of energy, viz. electricity and fossil fuels, such as coal, oil products and natural gas. The energy requirements of the unit operations were obtained from literature sources and were expressed as kWh per ton refined metal in the model. Using the mass balance and taking the efficiencies of the unit operations into account, the energy consumption per ton throughput could be determined. The energy needed for the production of reagents, fluxes etc. used is included in the total energy demand of the process (Eq. 5.23).

$$E_{Total} = Q_{in} \cdot E_{process} \cdot R_{process} \tag{5.23}$$

where:

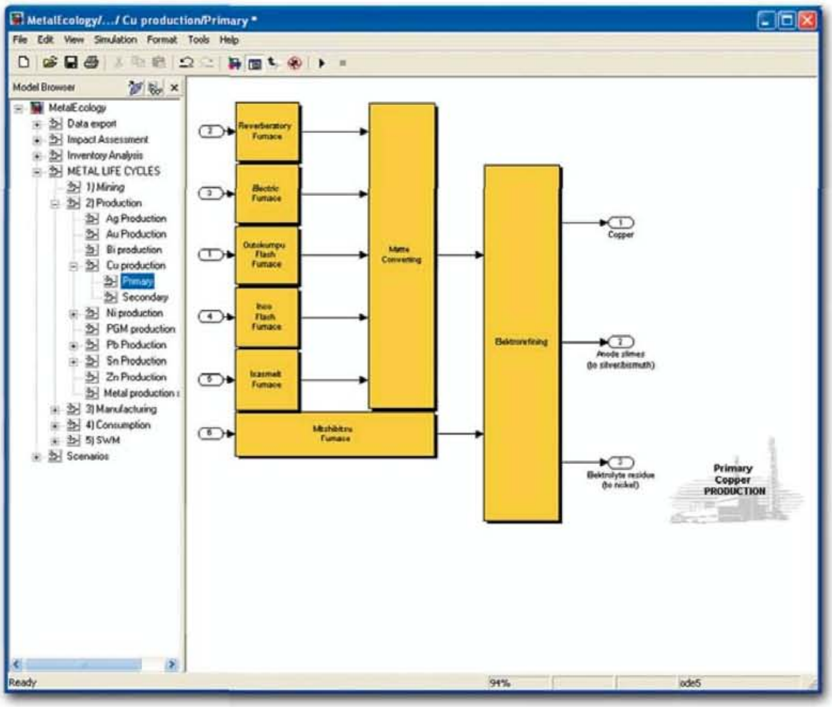


Figure 5.6: Copper production flowchart in Simulink™

Q_{in} = Process input in ton of metal (ton/a)
E_{Total} = Total energy requirement of the process (kWh/t)
$E_{process}$ = Energy requirements of the process based on the amount of end product that is produced from the input (kWh/t)
$R_{process}$ = Mass of end product that can be produced fromthe input (ton)

Level IV: Metal production flowcharts

The efficiency of the production and recycling of a certain metal - as well as the amount of waste and emissions produced in the process - is not constant, but is dependent on the production and recovery of other metals. To estimate environmental impacts, or the effects of dynamics, these interconnections must be taken into account. As the metal cycles are connected at the level of processes, the mining of metal ores, metal production and solid metal waste management stages in the model are constructed bottom-up (Figure 5.6).

According to the quantitative description of production and recovery of metals in Appendix B, the flowcharts for mining, production and solid waste management were constructed by interconnecting the input and output streams of the processes involved in the mining, production and recovery of that metal. As discussed in Chapter 5, two types of parameters determine dynamic material flows through flowcharts: process parameters and structural parameters

(Figure 5.2).

The *process parameters* ($p_{j,i}$) determine which part of the raw material is converted to product, intermediate, residue or emission in process step j. As described in the previous section, linear relationships between feed and process outputs were used to approximate the fundamental thermodynamics and physics in each production and process step. The product, $P_1(t)$, of a process j as function of time is given by process parameter, $p_{i,j}$, multiplied by its the feed.

Because metals are often produced through more than production route, a raw material, such as ore concentrate or crude metal, can be used in more than one process (the raw material in Figure 5.2 is used by three processes). The *structural parameters* (s_j) determine the flow of material through the different processing routes and thus the feed of the different processes. At any point in time, the feed of process 1 is given by multiplication of the supply of raw material at that time by structural parameter s_1. Distribution of the mass flows over the process routes was based on the literature. The partitioning of the elements over the mass flows was determined by dividing the average (reconciled) feed compositions by the total composition of raw materials (Eq. 5.24). Note that for primary material, new scrap and old scrap routes the structural parameters differ.

$$s_i = \frac{C_i \cdot f_i}{\sum_{i=1}^{n} C_i \cdot f_i} \tag{5.24}$$

where:

C_i = average reconciled feed composition of process i (ton/ton)
f_i = average use of raw materials of process i (ton/a)

Data reconciliation and extensive industrial knowledge obtained through reliable personal industry contacts, as well as extensive in-house knowledge ensured that the data is of high quality and reflects the current state-of-the-art.

Level III: Interconnected process flowcharts

After construction of the flowcharts for the individual metals, the flowcharts are linked through intermediates. The main intermediates are represented as orange blocks in Figure 5.7.

The amount of intermediate disposed of (R in the hypothetical flowchart, Figure 5.2) is determined by the demand for, and supply of intermediate. In order to avoid convergence problems that arose when using direct connection of the processes the interconnections between the material cycles were modelled as stocks. This ensures that the consumption of an intermediate is not affected by the (small) fluctuations in the production of the intermediate and allows for better (faster) convergence. Kleijn et al. [147] distinguish two basic types of relations between stocks and flows:

- The stock as a *size buffer*: In this approach, the outflow is proportional to the stock's magnitude. This is the case for the leaching of materials into groundwater from stocks such as heavy metals in landfills, or nitrate in soil. modelling this type of flow-stock relation is relatively straightforward. First, the magnitude of the stock has to be determined, for example, by measurements or by mass balance calculation based on records of past inflows and outflows. The outflow can then be calculated as a simple fraction of the stock leading to a geometric distribution. Most environmental stocks conform to this type (e.g. leachate models see Section 5.3.4), and some emissions from economic stocks

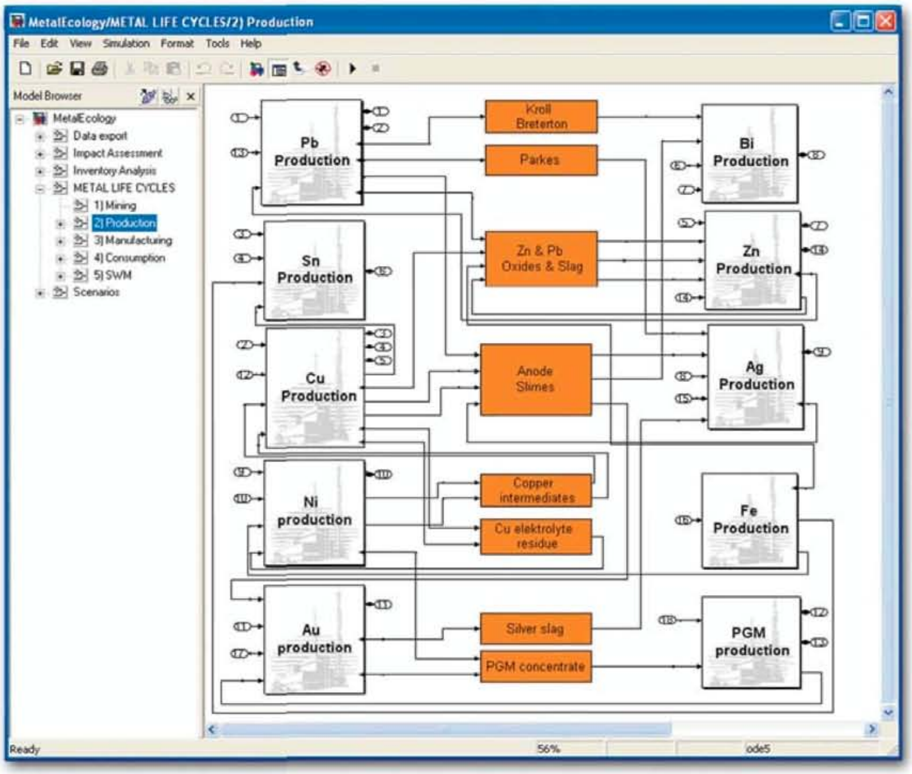


Figure 5.7: Interconnected metal production flowcharts in Simulink™

as well (e.g. dissipative use, Section 5.3.3). This type of model is also quite common in process design as a ideal "Continuously Stirred Tank Reactor" (CSTR) model, or as first order kinetics in chemical process control.

- The stock as a *time buffer*: In this approach, the outflow is a delayed inflow. An example is the modelling of waste flows from stocks of goods in society (see Section 5.3.3). Contrary to the nitrate example mentioned above, in this case it does make a difference at what point in time a certain product has entered the stock. Each individual product has a certain life span, and on average the older specimens will enter the waste stage earlier than the newer ones. Thus, not only the magnitude of the stock but also the age distribution of products in the stock determines the outflow.

For the modelling of the intermediates, it does not make a difference at what point in time a certain intermediate has entered the stock, it is rather its composition that determines its outflow: In general, the production of an intermediate is greater than the consumption of the intermediate. It is assumed that this overproduction is because not all intermediate is economical feasible to process. A decrease of the stock level means that economic less viable intermediates need to be processed as well, while an increase of stock indicates that only the economically attractive intermediates are processed. Moreover, a relatively short residence time (one year) in the stocks is assumed. The total mass flow and each element is given by Eqs. 5.25 to 5.28.

$$\varphi_{out,i}(t)' = S_i(t) \cdot \frac{1}{\tau} \tag{5.25}$$

$$R(t) = \varphi_{out,i}(t)' - \varphi_{out,i}(t) \tag{5.26}$$

$$\varphi_{out,i}(t) = \begin{cases} \varphi_{out,i}(t)' & if \quad \varphi_{out,i}(t)' < D_{I,i}(t) \\ D_{I,i} & if \quad \varphi_{out,i}(t)' \geq D_{I,i}(t) \end{cases} \tag{5.27}$$

$$S_i(t) = \int_0^t (\varphi_{in,i} - S_i(t) \cdot \frac{1}{\tau}) \cdot dt \tag{5.28}$$

where:

i = vector elements: total mass, Cu, Pb, Sn, Bi, Zn, Ag, Sb, As, Ni, Au, Pd, Cd, Fe, S (Co, Rh, Pt)
$\varphi_{in,i}(t)$ = production of intermediate vector element i (ton/a)
$\varphi_{out,i}(t)$ = consumption of intermediate vector element i (ton/a)
$\varphi_{out,i}(t)'$ = outflow of vector element i from intermediate stock (ton/a)
$R_i(t)$ = disposal of residue vector element i (ton/a)
$D_{I,i}(t)$ = demand for intermediate element i (ton/a)
τ = average residence time in intermediate stock (a)
$S_i(t)$ = quantity of i in intermediate stock (ton)

In the model, the primary raw material mix used for the production of a metal is fixed. However, if the supply of an intermediate decreases, this means the supply of other raw materials for the production must increase to meet the demand for that metal. It is assumed that the demand for the other raw materials increases, but their relative share remains constant. In case of a decreased supply of intermediate j, the total increase in other raw materials can be determined from Eqs. 5.29 and 5.30.

$$\Delta_{\text{int},i} = (D_{\text{int},i} - Su_{\text{int},i}) \cdot E_{\text{int},i} \tag{5.29}$$

$$\Delta D_{\text{int},j} = \frac{f_j}{1 - f_i} \cdot \Delta_{\text{int},i} \tag{5.30}$$

where:

$\Delta_{int,i}(t)$ = shortage of intermediate i (ton/a)
$D_{int,i}(t)$ = demand for intermediate i (ton/a)
$Su_{int,i}(t)$ = supply of intermediate i (ton/a)
$E_{int,i}$ = efficiency of metal production from intermediate i (-)
$\Delta D_{int,j}(t)$ = increase in demand for intermediate j (ton/a)
f_i = share of metal produced from other intermediate i (-)
f_j = share of metal produced from other intermediate j (-)

Note that these equations do not apply to all vector elements, but only to the metal produced from the intermediate and other raw materials.

Level III: Mining and concentration flowcharts

In the model, the demand for ore, D_{ore}, is determined by the total demand for metal, D'_{ore}, and the secondary material supplied to the market, S_{sec}. It is assumed that all of the secondary material is used (Eq. 5.31). The amount of ore required is calculated using the efficiency of the primary production routes and the efficiency of the ore processing process (Eq. 5.32). The supply of secondary materials is expressed in ton ores according to Eq. 5.33.

$$D_{ore}(t) = D'_{ore}(t) - S_{\text{sec.}}(t) \tag{5.31}$$

$$D'_{ore}(t) = \frac{D_{metal}(t)}{\sum_{i=1}^{n_i} (f_{op,i}(t) \cdot R_{op,i}) \cdot \sum_{j=1}^{n_j} (f_{pp,j}(t) \cdot R_{pp,j})} \tag{5.32}$$

$$S_{\text{sec.}}(t) = \frac{S_{\text{sec.}metal}(t) \cdot \sum_k f_{sp,k}(t) \cdot R_{sp,k}}{\sum_i f_{op,i}(t) \cdot R_{op,i} \cdot \sum_j f_{pp,j}(t) \cdot R_{pp,j}} \tag{5.33}$$

where:

$D_{ore}(t)$ = Demand for ore (ton_{ore}/a)
$S_{sec.}(t)$ = Supply of secondary material (ton_{ore}/a)
$D'_{ore}(t)$ = Demand for metal expressed in ore (ton_{ore}/a)
$D_{metal}(t)$ = Demand for metal ($\text{ton}_{\text{metal}}$/a)
$f_{op,i}(t)$ = Fraction of ore processed through route i (-/-)
$R_{op,i}$ = Efficiency of ore processing route i ($\text{ton}_{\text{concentrate}}/\text{ton}_{\text{ore}}$)
$f_{pp,j}(t)$ = Fraction of concentrate processed through route j (-/-)
$R_{pp,j}$ = Efficiency of primary production route j ($\text{ton}_{\text{concentrate}}/\text{ton}_{\text{ore}}$)
$S_{sec.metal}(t)$ = Supply of secondary material ($\text{ton}_{\text{waste}}$/a)
$f_{sp,k}(t)$ = Fraction of concentrate processed through route k (-/-)
$R_{sp,k}$ = Efficiency of primary production route k ($\text{ton}_{\text{metal}}/\text{ton}_{\text{waste}}$)

The processing of the ores converts the ores into concentrates and tailings (residues). The concentration (or "beneficiation") of the ores generally includes crushing of the rock followed by dense medium separation in which the light gangue material is separated from the more heavy pieces. Subsequently the separated materials are ground and further processed through flotation, in which the minerals are separated on their tendency to attach to air bubbles [239]. Because of the low concentration of the metals in the ores, each ton of metal concentrate involves the removal and processing of seven (zinc) to more than sixty tonnes of ore (tin). The ore processing is described with linear models based on reconciled mass balances (see "The mass balance of a process" in Section 5.3.3). The processing of a single ore may produce different types of concentrates. As illustrated in the metal wheel (Chapter 3), ores typically contain more than one metal. Lead, zinc and copper are often present in lead and zinc ores. Lead is predominately mined from combined lead-zinc ores. Seventy per cent of lead is mined together with zinc, and only twenty per cent of the lead concentrate production comes from dedicated lead mines. The remainder is produced as by-product from zinc mining. In the model, therefore, it is assumed that all lead and zinc are produced from the same ore, which also produces a copper concentrate. In some cases, "co-metals" are not separated in the mining and concentration of ores, but recovered further downstream the metal production chains. Concentrates that contain zinc, lead and cadmium are processed in the Imperial Smelting Furnace that produces lead bullion, and zinc-cadmium concentrate. Silver is produced from dedicated silver ores, but also from by-products of lead (zinc), copper and gold production. For these metals, Eq. 5.31 also includes the supply of metals from intermediates (Eq. 5.34). The demand for these intermediates is fixed fraction of the total demand for the metal (Eq. 5.35).

$$D_{ore}(t) = D'_{ore}(t) - S_{sec.}(t) - S_{i.m.}(t) \tag{5.34}$$

$$S_{i.m.}(t) = \sum_{l=1}^{n_l} \left(\frac{f_{i.m.,l}(t)}{R_{i.m.,l}} \right) \cdot \frac{D_{metal}(t)}{\sum\limits_{i=1}^{n_i} \left(f_{op,i}(t) \cdot R_{op,i} \right) \cdot \sum\limits_{j=1}^{n_j} \left(f_{pp,j}(t) \cdot R_{pp,j} \right)} \tag{5.35}$$

where:

$S_{i.m.}$ = Supply of intermediates ($\mathrm{ton}_{\mathrm{ore}}/\mathrm{a}$)
$f_{i.m.,l}$ = Fraction of intermediate processed through route l (-/-)
$R_{i.m.,l}$ = Efficiency of intermediate production route l ($\mathrm{ton}_{\mathrm{metal}}/\mathrm{ton}_{\mathrm{interm.}}$)

Level III: Manufacturing and consumption flowcharts

To estimate the old scrap from the consumption phase, the stock is modelled as a time buffer (after Klein et al. [147]). Each individual product has a certain life span, and on average the older specimens will enter the waste stage earlier than the newer ones. Thus, not only the magnitude of the stock but also the age distribution of products in the stock determines the outflow. The relation between the present size of the stocks and the future emissions and waste flows is often not straightforward and can not be modelled easily [147, 234]. This is even more true when considering that the societal stock of metals consists of a large number of products with widely varying life spans. The problem with this model type is that to estimate waste flows, product compositions and quantities as well as the life span distribution must be obtained for these products. In some cases - as in the case of cars - detailed data are available in statistics (see e.g. Van Schaik and Reuter [2]) and input distributions can be obtained from real data. However, often this is not the case and assumptions are required.

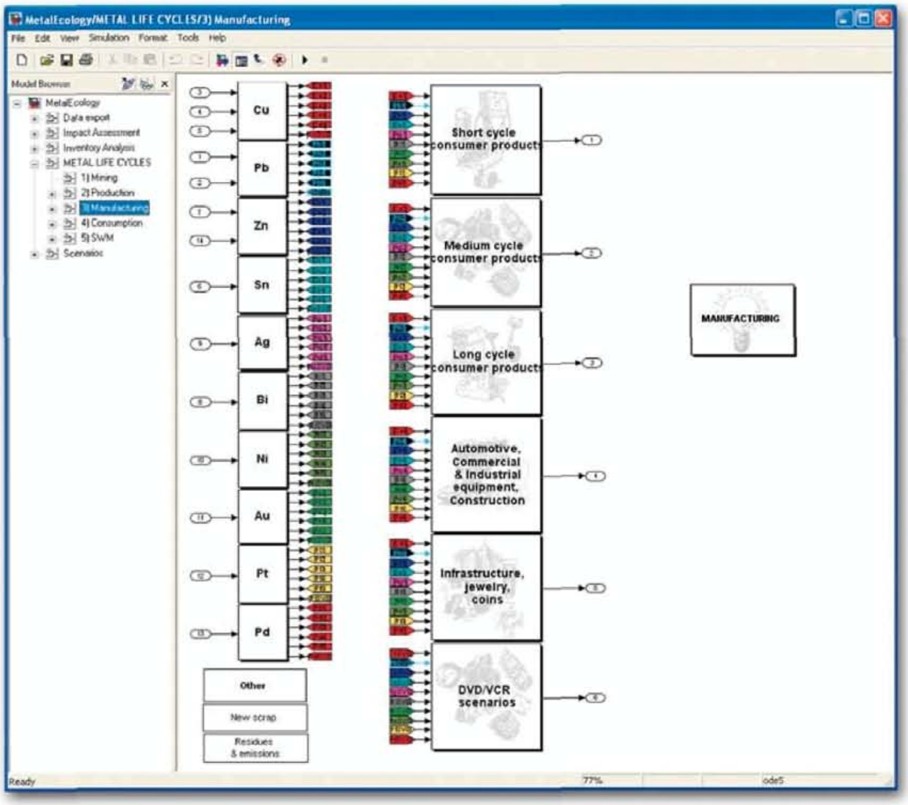


Figure 5.8: Product manufacture model in Simulink™

In the model, five different (hypothetical) products are manufactured that have different average lifespans (see Figure 5.8)[1]. In the manufacture of products, all seventeen elements are considered. The distribution of the elements over the five products is estimated based on their end uses. As the end uses change over time, these fractions are a function of time as well. The compositions of the products are calculated by the element-wise multiplication of the vector that contains the total production and the production of individual elements, by the vector containing the distribution fractions for the total and individual elements. The compositions of the five hypothetical products, CPrI-V, are given by division of all of the elements of vector PrI-V by the total manufacture of the product, viz. the first vector element (Eqs. 5.36 and 5.37):

$$\mathrm{Pr}_j(t) = f_j(t) \cdot P_m(t) \tag{5.36}$$

$$C_{\mathrm{Pr}\,j}(t) = \frac{\mathrm{Pr}_j(t)}{\mathrm{Pr}_{j,1}(t)} \tag{5.37}$$

where:

$\mathrm{Pr}_{j,j}(t)$ = Manufacture of product j (ton/a)
$f_i(t)$ = Fractions of the elements manufactured as product j (-/-)
$P_{m,j}(t)$ = Element i of the production vector of metal m (ton/a)
$C_{\mathrm{Pr}\,j}(t)$ = Composition of product j (ton/ton)

The first element of vector, $\mathrm{Pr}_{j,j}(t)$, is the total quantity of product j, which is the sum of all other elements (2-18) in the vector. For the co-elements that have no production system production vector, $P_{m,j}(t)$, is the demand for the element, D_{metal}. The generation of new scrap of metal i in the manufacture of product j is then given by Eq. 5.38.

$$NS_{j,i}(t) = P_i(t) \cdot f_{ns,i} \cdot f_j(t) \tag{5.38}$$

To approximate the lifespan distribution, most commonplace would be to use a normal (or Gaussian) distribution, which is used by Baccini and Bader [232] as an example of life span distribution. Despite of the fact that the normal distribution is most commonly observed in natural and social behaviour, the choice for a normal distribution is arbitrary. In some cases, there are arguments for another type of distribution. Skewed distributions such as Weibull's, which is already used in lifetime modelling (e.g. Van Schaik and Reuter [2]), might sometimes be more appropriate. Considering that the five hypothetical products consist of many different products that each have distributed life spans, arguments for other distributions are difficult to give. Therefore, the life spans of the products are assumed to be normally distributed around a mean, μ. The outflow of discarded products, W_j, from the at time t of product j produced at time t_i is given by Eq. 5.39.

$$W_{j,i}(t) = \mathrm{Pr}_j(t_i) \cdot \frac{e^{\frac{(t-t_i-\mu_j)^2}{(2\sigma_j)^2}}}{\sigma_j\sqrt{2\pi}} \tag{5.39}$$

The total waste generated from product j produced at time t is then given by Eq. 5.40.

$$W_j(t) = \int_{i=t}^{i=0} \mathrm{Pr}_j(t_i) \cdot \frac{e^{\frac{-(t-t_i-\mu_j)^2}{(2\sigma_j)^2}}}{\sigma_j\sqrt{2\pi}} \cdot dt \tag{5.40}$$

---

[1] Note that that in Figure 5.8 a sixth product is included; this additional product is only used for DVD/VCR scenarios.

where:

$W_j(t)$ = The discarded product j at time t (ton)
$\mathrm{Pr}_j(t_i)$ = Manufacture of product j at time t_i (ton)
μ_j = Average life span of product j
σ_j = Average distribution in the life span of product j

For simulation in Simulink™, the normal distribution was discretized using the variable delay blocks in Simulink™. Hereto, the normal distribution curve from $\mu - 3\sigma$ to $\mu + 3\sigma$ (representing ca. 99.7% of the total surface of the normal distribution curve) was divided into eleven slices (Figure 5.9). The surface of each slice surface was calculated, and normalized so that the sum of all surfaces equals one. In Simulink™, the distributed delay system consists of eleven delay blocks with a delay of τ_1 to τ_{11}, to which one of the partitions, $f_{\tau=1}$ to $f_{\tau=11}$, is allocated (Eqs. 5.41 to 5.43).

$$W_j(t) = \sum_{\tau_{j,n}=\tau_{j,1}}^{\tau_{j,n}=\tau_{j,11}} \mathrm{Pr}_j(t-\tau_{j,n})\cdot f_{\tau_{j,n}} \tag{5.41}$$

$$\tau_{j,n} = \mu_j - (3\tfrac{3}{11} - n\cdot\tfrac{6}{11})\sigma_j \tag{5.42}$$

$$f_{\tau_{j,n}} = \frac{\int\limits_{\mu_j-3\sigma_j+n*\frac{6}{11}\sigma_j}^{\mu_j-3\sigma_j+(n-1)*\frac{6}{11}\sigma_j}\left(\frac{e^{\left(\frac{-(t-\mu_j)^2}{(2\sigma_j)^2}\right)}}{\sigma_j\sqrt{2\pi}}\right)}{\int\limits_{\mu_j-3\sigma_j}^{\mu_j+3\sigma_j}\left(\frac{e^{\left(\frac{-(t-\mu_j)^2}{(2\sigma_j)^2}\right)}}{\sigma_j\sqrt{2\pi}}\right)} \tag{5.43}$$

New scrap refers to metal discards generated within an industrial setting, either at metal producers ("home scrap") or from product manufacturers ("prompt industrial scrap"). Because new scrap stays within the mill or factory, the quality (i.e. chemical composition) is generally well known and homogeneous. As a result, this metal readily returns to the production loop. Eq. 5.44 shows the new scrap generation calculation.

$$NS_i(t) = P_i(t)\cdot f_{ns,i} \tag{5.44}$$

where:

$NS_i(t)$ = New scrap generation (ton/a)
$P_i(t)$ = Production of metal i (ton/a)
$f_{ns,i}$ = Fraction metal i rejected as new scrap in product manufacture

Residues from manufacture and consumption include new scrap, other manufacturing residues and emissions due to dissipative use. In the model of the manufacturing process, a fixed fraction of each metal is returned to the metal production system as new scrap with a delay of time step (0.05 year, to "break" the algebraic loop). It is assumed that the new scrap is remelted without material losses; the composition of the new scrap is identical to the refined metal. Many of the losses in the metal resource cycle end up in mine wastes (gangue), metal production slags, or and in metal-containing products and waste processing residues that are disposed of on landfills. Some of this metal could conceivably be recovered in the future as technology improves. However, there are also routes by which metals during consumption are converted into unrecoverable forms and dissipated into the environment. These

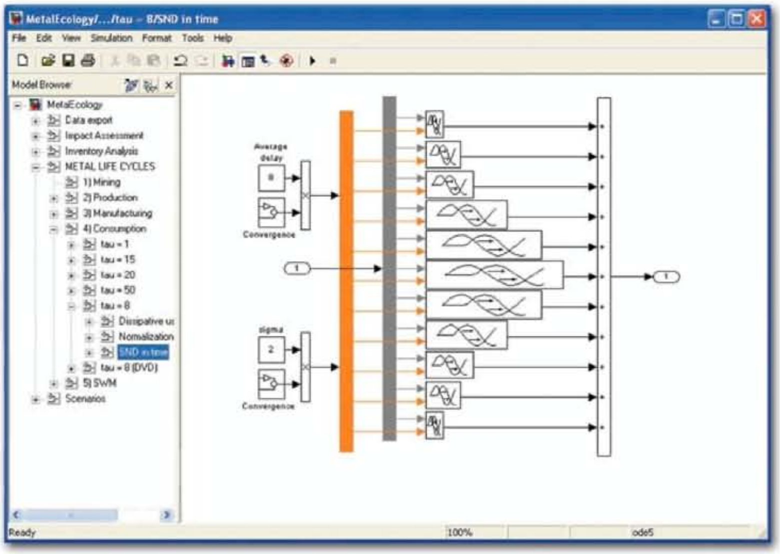


Figure 5.9: Normal distribution delay in Simulink™

are via te consumption of food, the use of chemicals, corrosion and erosion. These losses are a deliberate or unavoidable (with current technology) consequence of product use, and are referred to as dissipative use of materials [240]. Dissipative use comprises two components viz. (i) direct dissipative uses such as fertilizers and manure spread on fields, and salt spread on roads, and (ii) dissipative losses such as rubber worn away from car tires, particles worn from friction products such as brakes and clutches, and solvents used in paints or other coatings. Dissipative uses can be part of an ultimate throughput (e.g. mineral fertilizer or other agricultural chemicals) or part of recycling (e.g. manure, compost, and sewage applied on fields for nutrient recycling). The discarded product flow, W_j, must be corrected for dissipative use (Eq. 5.45). The fraction of dissipative use of each metal is based on [227, 241], and is given in the quantitative description of the metal cycles (see Figure 5.9).

$$W'_j(t) = \sum_{i=1}^{n}(1 - f_{dissipation,i}) \cdot W_{j,i}(t) \tag{5.45}$$

where:

$f_{dissipation}$ = The vector containing the fractions dissipative use of each metal (ton/ton)

$W'_j(t)$ = Flow of discarded product j corrected for dissipative use (ton/a)

The losses of direct dissipative use can be considered equally distributed over the average lifespan of a product: Fertilizer is spread onto land, and dissipates into the environment. Once the stock of fertilizer is used, new fertilizer is bought. For dissipative losses, such as corrosion and erosion, can also be assumed to be more or less constant over time (see e.g. discussion on the wear of copper pipes in Ayres et al. [241]). Dissipative use can thus be modelled using the ***stock as a size buffer*** approach, where the outflow is proportional to the stock's magnitude. The dissipation rate is a function of the stock dissipated metal $C_{j,diss,stock}$, the fraction dissipative use, $f_{dissipation}$, and the average lifespan of product j, τ_j (Eqs. 5.46 and 5.47). The consumed stock of metals contained product j, $C_{j,stock}$, is then given by Eq. 5.48.

$$D_j(t) = \sum_{i=1}^{n} \frac{f_{dissipation,i}}{\tau_{j,i}} \cdot C_{j,i,diss,stock} \tag{5.46}$$

$$C_{j,diss,stock}(t) = \sum_{i=1}^{n} \int_{t}^{0} (f_{dissipation,i} \cdot W'_{j,i}(t) - D_{j,i}(t)) \cdot dt \tag{5.47}$$

$$C_{j,stock}(t) = \int_{t}^{0} (Pr_j(t) - W'_j(t) - D_j(t)) \cdot dt \tag{5.48}$$

where:

C_{stock} = Vector of the stock of product j in use (ton)
τ_j = Average life span of product j (a)

Level III: Solid waste management flowchart

Figure 5.10 shows the different waste management routes included in the model. The metals, which are not recovered through the municipal solid waste, electrical and electronic appliances, end-of-life vehicles and construction and demolition waste routes, are partly processed through the "other" route. As this route is an aggregate of all other routes through which metals are recovered, it is difficult to estimate composition and quantity of the metal concentrates produced in this route. Under the block "Scrap dealer" all the other routes are included as "Other routes".

The composition of the produced secondary resources is dependent on the physical and chemical combinations in the products, and the carrier metal in the recovery. Circuitry boards for example are typically recovered for the copper value. Copper is the carrier metal for these products, and the co-elements in the copper concentrate are typically recovered in the copper production circuit. Based on the distribution of the metals over the different products and information on their subsequent recovery, the distribution of metals over the waste flows was estimated. The quantity of the metals recovered through this route could be estimated based on the global metal recycling rates. The Subtraction of the amount of metals, that are recycled through these four routes, from the global amount recycled metals, gives the recycling of metals through the "other" route.

5.3.4 Interpretation and impacts assessment

In the model two ways of interpretation of the results are included (see Chapter 3):

- SFA-type indicators: these are typically defined in terms of flows and accumulations of the material(s) under study. Indicators can also be more elaborate, by calculating compound indicators relative to the management of the whole chain. For example, one can focus on the efficiency of processes or groups of processes in terms of the ratio between the production of the desired output related to the magnitude of the input of the process, or to the amount of the produced waste.

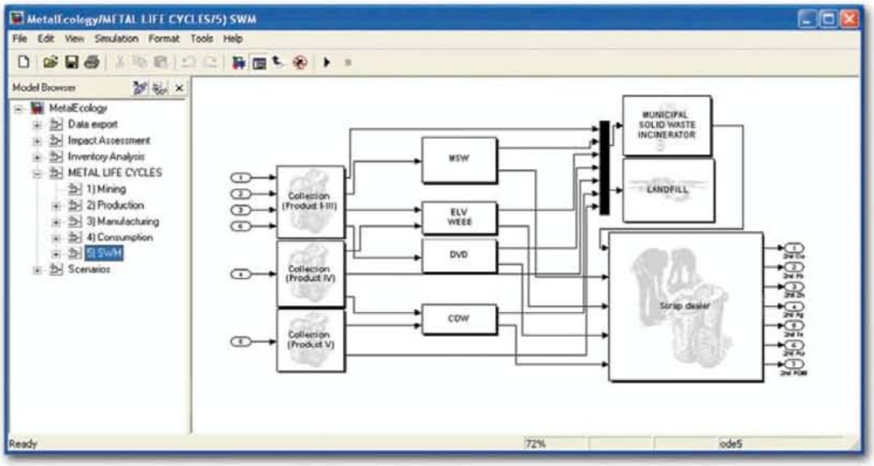
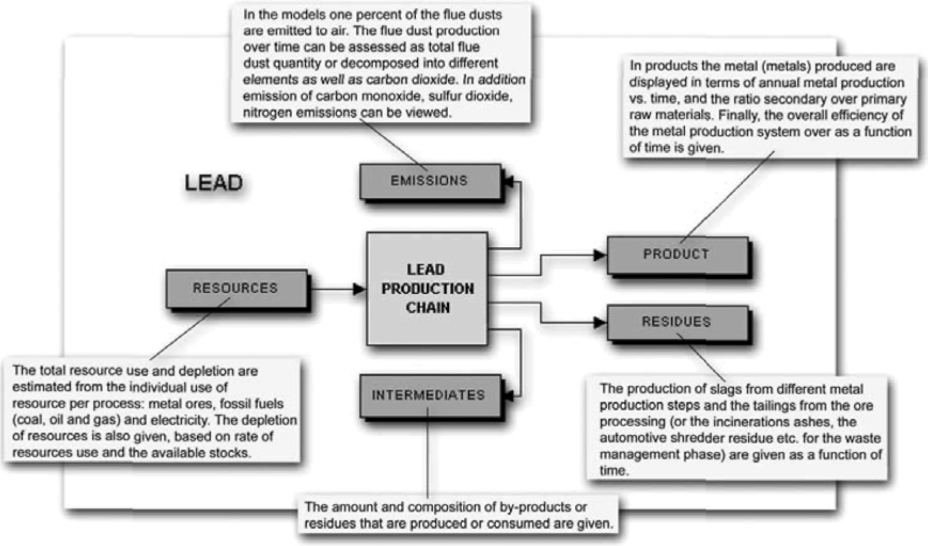


Figure 5.10: Waste management flowchart in Simulink™

- LCA-type impact assessment indicators: in these indicators outputs to the environment are assigned to a number of environmental issues or environmental impact categories, such as global warming, ozone depletion, and acidification.

LCA-type impact assessment

To allow simple interpretation, and because impacts assessment is as yet not well developed in MFA [41], a commercial LCA impact assessment package was included in the approach. The Eco-indicator 99 method [242] was adopted as an indicator for environmental impacts. LCA results per simulation can obtained as single score, as damages (human health, ecosystem quality and resource depletion) or the various environmental themes. It should be noted, that because LCA does not consider time dependency, the effects of the damage over time, e.g. the actual resource depletion, are not accounted for. In other words, if metals ores are mined over time, the available stocks decrease and the seriousness of further depletion increases. In the LCA impact assessment, the increasing damage of resource consumption is not accounted for. After disposal on landfills metals slowly leach out, which results in environmental hazards to soil and groundwater. In the model, based on leaching numbers, the total amount of metal leached out over a time span of 100 years waste used to determine the environmental impact of these emissions, rather than simulation of the leach process over time. It was assumed that the bulk, being 90% of the total amount of metal, adheres to the soil, and that 10% of the total amount of metal leached out reports to the groundwater. This is not included in the impact assessment. This is an important difference with MFA, which should be realized when interpreting the impact assessment results.



In the models one percent of the flue dusts are emitted to air. The flue dust production over time can be assessed as total flue dust quantity or decomposed into different *elements as well as carbon dioxide. In addition* emission of carbon monoxide, sulfur dioxide, nitrogen emissions can be viewed.

In products the metal (metals) produced are displayed in terms of annual metal production vs. time, and the ratio secondary over primary raw materials. Finally, the overall efficiency of the metal production system over as a function of time is given.

The total resource use and depletion are estimated from the individual use of resource per process: metal ores, fossil fuels (coal, oil and gas) and electricity. The depletion of resources is also given, based on rate of resources use and the available stocks.

The production of slags from different metal production steps and the tailings from the ore processing (or the incinerations ashes, the automotive shredder residue etc. for the waste management phase) are given as a function of time.

The amount and composition of by-products or residues that are produced or consumed are given.

Figure 5.11: An example of the result analysis card of a metal production chain

Allocation of burdens

In addition assessment of the total impacts, the model also allows for a detailed more detailed analysis: The environmental impacts of each metal production chain individually. In impacts assessment the environmental burdens, such as wastes and emissions, are allocated to products. Here, a methodological problem arises. Metal production processes can belong to more than one production system, e.g. in copper production also raw materials for silver production are generated. The problem is to decide what share of the environmental burden should be allocated to the metal investigated. The model can calculate the environmental impact of the total interconnected metal life cycles, or each cycle individual based on mass allocation (see Van Tweel [151] for an extensive description of the allocation procedures).

Dynamic data analysis

A dynamic MFA simulates the effect of future developments on the system and its environment. Rather than indicating damage scores due to resource depletion alone, the model can shows a decrease of the available resource stock in a given scenario. The results (the stocks and flows in time) of simulations are then available for detailed analysis. For each simulation, the total inventory as a function of time can be accessed (and saved). In addition, the inventory tables of the subsystems can also be accessed individually. This can assist interpretation of the LCA values. Moreover, when e.g. flue dusts, ore extraction or sulphur dioxide production of the total system, and of the individual production chains have been calculated, the need for improvement can be discussed using the quantitative information generated. There are several procedures included in the model for doing this. At the level of processes, important flows can be analyzed using the scope block (during and after simulation).

For each production chain, or resource stage the overall resource use, airborne emissions, residues intermediates and products can be accessed through score cards (Figure 5.11):

- Resources: The total resource use and depletion are estimated from the individual use of resource per process: metal ores, fossil fuels (coal, oil and gas) and electricity. The depletion of resources is also given, based on rate of resources use and the available stocks.
- Emissions: In the models one percent of the flue dusts are emitted to air. The flue dust production over time can be assessed as total flue dust quantity or decomposed into different elements as well as carbon dioxide. In addition emission of carbon monoxide, sulphur dioxide, nitrogen emissions can be viewed.
- Products: In products the metal (metals) produced are displayed in terms of annual metal production vs. time, and the ratio secondary over primary raw materials. Finally, the overall efficiency of the metal production system over as a function of time is given
- Intermediates: the amount of by-products or residues that are produced or consumed is given.
- Residues: The production of slags from different metal production steps and the tailings from the ore processing (or the incinerations ashes, the automotive shredder residue etc. for the waste management phase) are given as a function of time.

Leachate models

For the complete model also the leaching of materials into the environmental compartment soil and water is calculated.

Time dependency in landfills The disposal of wastes leads to emissions into the environment. Some emissions occur directly at the processing of waste, such as the emissions into the air resulting from the incineration of waste. Other emissions typically occur after the disposal processes: When the solid waste comes into contact with water, such as infiltrating rain water or groundwater, metals dissolve and leach out. Due to disposal of EOL wastes, incineration ashes and flue dusts, and production residues on landfills metals and other substances leach into soil and groundwater long after their disposal. The leaching rate changes over time. For example, Finnveden [243], and later Finnveden and Nielsen [244] distinguish between leachate rate during a surveyable period and a (hypothetical) infinite period. The surveyable time corresponds to the time until a pseudo steady state is reached in the landfill, which is probably in the magnitude of 100 years. Only a small fraction of the landfilled metals is expected to be emitted during the first century, typically between 0.001 and 0.1% of the metal in the landfill body. Emissions from landfills may prevail for a very long time, often thousands of years or longer. It is therefore assumed that material remaining after the surveyable time is completely emitted during the infinite period [244]. This approach is used in the ORWARE waste management model for example. Here the leachate rate is proportional to two stocks, viz. the non steady state stock (surveyable time) and a steady state stock (infinite time). The choice for the distinction between two time frames (and thus stocks in the model) appears somewhat arbitrary [245][2]. With knowledge of the different decomposition processes in the

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[2] In this publication ORWARE is described as a compromise to compare the slowly released emissions from the landfill with the instant emissions from the other processes in the system

landfill, a series of typical phases can be distinguished (see e.g. Farquhar and Rovers [246], Ehrig [247], Chian et al. [248] and Christensen and Kjeldsen [249]). However, typically five phases are distinguished. In addition, the remaining metals may not only leach out, but can also be immobilized in the landfill. The long-term behaviour of a landfill is strongly influenced by a large number of factors, including content of organic material, moisture, oxygen, and pH. In general the knowledge of the long-term fate of contaminants in landfills and its relation to waste processes is insufficient for detailed modelling (see e.g. Bozkurt et al. [250, 251]), in particular at global scale considering the differences in local conditions and landfill practice.

In the model, the leachate is simply assumed to be proportional to the stock of materials in landfills (after Kleijn et al. [147]). The leachate can then be calculated as a simple fraction of the landfill stock (Eq. 5.49 and 5.50).

$$L(t) = R_l \cdot LF_{stock}(t) \tag{5.49}$$

$$LF_{stock}(t) = \int_0^t \sum_{j=1}^{j=V} f_{landfill,j} \cdot W_j'(t) - L(t) \cdot dt \tag{5.50}$$

where:

$L(t)$ = Leachate of metals and other substances (ton/a)
R_l = Leachate rate (ton/ton a)
$LF_{stock}(t)$ = Stock of wastes disposed of on landfills (ton)
$f_{landfill,j}(t)$ = Fraction of Waste j disposed of on landfills (ton/ton)

Different leachate rates are included for the different types of waste. In the model, two types of landfills for EOL products are included representing the extremes in landfilling practice around the world: (i) Sanitary landfills that employ leachate containment, collection, and treatment, and (ii) uncontrolled landfills that do not. For uncontrolled landfills, the leachate rate is assumed to be ten times that of sanitary landfills (i.e. collection and containment efficiency of ninety per cent). The slag and tailings produced in the metal production system are separately disposed of on controlled landfills . Emissions into soil and groundwater (the leachate) from slag and tailings differ from those from household waste. In addition, the disposal of fly ash and bottom ash is modelled separately. Metals in fly ash occur mainly as salts, and therefore have higher leachability. The leachate rate is given by the fraction of material leached in the surveyable time divided by the period for which leaching of metals was determined. The metals that leach from the landfill body, distribute over soil and groundwater as 90:10. Note that the landfill models do not include leachate purification and landfill gas generation. At sanitary landfills, leachate is led to the municipal sewer system and treated in a conventional sewage treatment plant, or the leachate is treated separately, as it often contains higher levels of pollutants than ordinary sewage, and may require special purification methods. The process of leachate treatment is not included in the model. It is assumed to be disposed of on landfills. The metals flows are considered inert with respect to landfill gas emissions and these are not considered in the model as this emission of metal is very small compared to the other flows to air[3].

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[3] This is contrast to some authors that claim that some metals partly follow the landfill gas.

Transport

Metals, metal and ore concentrates, and intermediates are traded globally. Consequently, the distance between ore mining sites, metal production facilities, product manufacturers, consumers and waste processing facilities can be very large. Thus, it can be seen that transport plays an important role in the metal ecology , and is an important source of emissions and consumer of fossil fuels. Data on transport distances of metals, metal and ore concentrates, and intermediates was not found in literature, and had to be estimated. Statistics on the location of mines, metal production facilities and trade of metal and metal scrap was available from metal statistics [229]. A simplified model to estimate the transport distances from this data was used, based on a number of assumptions:

- transport occurs only between different stages in the metal life cycles, and in the waste management stage;
- transport distances can be estimated from the average distances between countries mining metal ore and countries producing the crude metals, and the import and export data of unwrought refined metal and alloys, and of metal scrap;[4]
- metals, metal and ore concentrates, and intermediates are traded first within the continents (Europe, North-America, South-America, Africa, Oceania, and Asia), and second between continents;

The distances between countries were obtained from CEPII [252]. These distances were estimated based on the longitudes and latitudes of the capitals using the great-circle formula from spherical trigonometry. To estimate emissions and fuel consumption resulting from the transport over these distances, transport was assumed to occur only over land or sea. Four modes of transport were considered: hauling with garbage truck, transport by truck, truck and trailer, tanker. Average figures for emissions and fuel consumption for the different modes of transportation (garbage truck, truck and bulk carrier) were obtained from literature (Rydh and Karlström [253], Bos [254], Kristensen [255] and Bruch et al. [256]). It was assumed that the bulk (95%) of intercontinental trade was transported over sea, and half of the intra-continental trade. Trucks with and without trailer equally carried the remaining load. Garbage trucks were only used in the collection of waste in the solid waste management phase. The effects of these assumptions on model outcomes were tested in the model sensitivity analysis [150].

5.3.5 Simulations

To investigate the feasibility and environmental impacts of changes to lead production on the metal ecology, the model allows two operating modes (i) An equilibrium (or quasi-dynamic) and (ii) a dynamic mode. The equilibrium mode can be used for ceteris paribus scenarios in which in this case only the effect of substitution of lead in solders is investigated. The dynamic mode also allows changing composition of waste composition and quantity, change in metal demand and metal recovery over time. A simplified illustration of a simulation scenario is depicted in Figure 5.12. The environmental impact (based on the Eco-Indicator 99, see Section 5.4.3) can be measured for an individual metal resource cycle, or for the interconnected resource cycles as a whole.

Because of the interconnectedness and dynamics present in the world metals production system, changes trickles through the system and results in different resource demands, different

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[4] The distances for waste management were estimated based on the situation in the Netherlands.

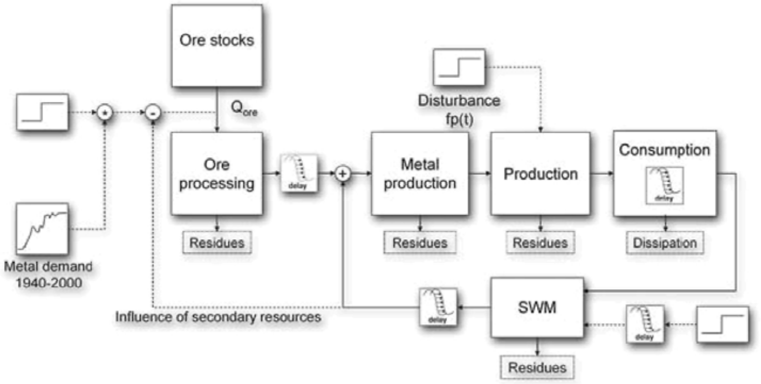

Figure 5.12: Simplified illustration of the lead-free scenarios in the dynamic model

amounts of intermediate disposed of or further processed, and different emissions. This can be easily seen using the lead-free solders, that are investigated as an example of a detoxification strategy below (Section 5.4). For the lead-free solder scenarios, the equilibrium mode is used. Figure 5.12 shows the disturbance of the equilibrium conditions as a result of the substitution. In order to obtain acceptable solder characteristics, lead-free solder is not simply tin without lead, but a new tin alloy that can contain different amounts of silver and copper, zinc, bismuth and antimony as argued above. Substitution would, therefore, affect both the interconnected metal cycles of the original and the new materials. The introduction of lead-free solder thus disturbs the demand for the different metals ($f_m(t)$): Lead demand declines, and tin demand increases due the higher tin content of the lead-free solders investigated. Dependent on substitute solders, the demand for bismuth, copper, zinc, silver and antimony rises. Furthermore, the solder substitution disturbs the distribution of metals over the different product categories ($f_p(t)$), and disturbs the waste management and recovery of the metals ($f_w(t)$). Over time, a decreasing amount of lead is collected as electronic wastes. Furthermore, since electronics are mainly recovered through the copper circuit, the substitution also affects the recovery/recycling routes of lead and the substitute metals.

The metal waste generation in 2000 in the equilibrium mode is estimated based on a simulation in the dynamic mode of the production of metals from 1940-2000 and their estimated residence times (or delays) in the consumption stage of the resource cycle during that period. Hereto the dynamic simulation starts at $t = 1940$, at which products are assumed to be produced only from virgin ore material ($Q_{ore} = Q_{demand}$). From $t = 1940$ to $t = 2000$ the model simulates the global metal production network, based on global metal production data, end-use of metals and recycling rates. In this period, the system converges to the actual state in 2000. The materials accumulate in the consumption stage and are assumed to reach the actual system material stocks. The secondary raw material stream partly replaces the primary concentrate according to the current recycling levels.

Except for the delay in the consumption phase, and in waste management all other delays were assumed negligible. At the time of substitution of lead for example, the metal demands is disturbed stepwise, as is the distribution of the metals over the products. Figure 5.12 shows that the change in metal over the different wastes in the solid waste management, $f_w(t)$, is delayed as well. Because of the normally distributed delay assumed for the products in consumption phase, the fraction of metal partitioned to a waste slowly changes over time. Apart from the consumption and waste management, time delays are only included in the model to break "algebraic loops"[5], which severely slow down and complicate simulation. These delays are one time step.

5.4 Detoxification strategy - lead-free solders

Solder is used throughout the manufacture of electrical and electronic equipment. The toxicity hazards of lead, particularly in end-of-life processing of electrical and electronic equipment, have led the European Union to develop a directive on the restriction of the use of certain substances in these products [225]. More specifically, the proposed directive stipulates the substitution of lead in consumer electronics to reduce emissions associated with lead content of landfills. Lead on landfills poses a risk to health and environment through leaching and consequently exposure through groundwater. Most of the lead in landfills in Europe originates from wasted electrical and electronic equipment (WEEE), and similar trends were observed in the U.S. However, most of the lead was found to originate from cathode ray tubes [257, 258, 259].

In the case study described below, the effect of lead elimination in solders for electronics on the global metal cycles is investigated. The possible changes in the metallurgical system underlying the introduction of lead-free solder are not known to all environmentalists, industrial ecologists and legislators, but this type of systems knowledge is necessary to co-ordinate decision-making across the resource cycles. The study investigates how the phase-out of lead influences the operation of the resource cycles, and how this affects the different stakeholders. For example, how effective is the directive in terms of prudent resource management, and the environmental impacts of the metal resource cycles? What problems can be expected with implementation of the directive, and thus which additional measures may be required from the legislators and policy-makers? How do changes in the operation of the resource cycles influence the environmental impacts of the lead-free alternatives? What problems can be expected for metallurgists? Lead substitution affects the configuration of the metal production system, and thus may lead to shortages of raw materials, or different environmental performance of metal production. In the next sections it will be shown that the underlying dynamics in the metal resource cycles must thus be understood, to evaluate the environmental impact and feasibility of the alternatives. As such, it provides a basis for policy on lead-free solders, or a basis for Life Cycle Analysis (LCA, see Chapter 2) studies on the phase-out of lead from electronic products .

5.4.1 Lead-free solders options

A relatively large number of lead free solders have been proposed so far, by researchers and manufacturers. Abtew et al. [260] counted approximately 70 candidates and Miric [261]

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[5] An algebraic loop generally occurs when an input port with "direct feedthrough" is driven by the output of the same block, either directly, or by a feedback path through other blocks with direct feedthrough. Direct feedthrough means that the output of these blocks can not be computed without knowing the values of the signals entering the blocks at these input ports.

counted 100 patents for lead free solder alloys. The ultimate goal of lead-free soldering research is finding a universal "drop in" replacement. Despite considerable research efforts for most applications, no single solder appears as suitable as the mainstream lead-based solder. The main substitute alloys are alloys based on tin as primary constituent with smaller additions of mainly silver and/or copper and, especially in Japan, bismuth. Besides these main substitutes, there are other alloys containing a wide variety of other metals like zinc, aluminium, nickel, antimony, germanium or indium. Indium appears because of its scarcity only an option in niche markets, rather than a substitute for lead in the mainstream solder alloys.

Table 5.3: Compositions and characteristics of the lead free solders considered.

Solder type	Cost[a] (€/kg)	Composition (%) Sn	Pb	Bi	Sb	Cu	Ag	Zn
SnPb	2.5	60	40					
SnAgCu	9.1	95.5				0.7	3.8	
SnCu	3.9	99.25				0.75		
SnAgSbBi	5.5	92		5	2		1	
SnZnBi	4.7	78		19				3
SnZn	3.6	91						9

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[a] Cost of a solder estimated based on the LME prices of metals (9/2002)

The IDEALS Project (1996-1999)[262] was a landmark collaborative European lead-free soldering project that for the first time evaluated lead-free soldering assembly under real-life conditions. In the project it was found that lead-free soldering technology based on SnAgCu(Sb) and SnBiSbAg alloys is technically and industrially viable. The selection of the lead-free alloys investigated in this study was made in collaboration with Philips (a large European consumer electronics manufacturer participating in the IDEALS project). Table 5.3 lists the solders investigated. A common solder alloy of 60% tin and 40% lead is used as a reference. Two binary solders are included representing the least expensive solder alloys, viz. tin-zinc and tin-copper alloys. A tin-zinc-bismuth alloy is included, which has a melting point close to the mainstream solders. In addition, two copper-silver-tin alloys are included: silver-bismuth-antimony-tin alloy and copper-silver-tin alloy[6]. To illustrate the dynamics, it is assumed that all alternative solders in Table 5.3 represent universal "drop in" replacements. In addition, it is assumed that these solders substitute all tin lead solders in a stepwise fashion. A stepwise introduction is chosen as this is the most extreme scenario; the effects of substitution are clearly visible, and easy to relate to the point of substitution.

5.4.2 Metallurgist

As mentioned before, only a small fraction of lead is substituted - solder for electronics accounts for only 1.5% of the lead production on a present year basis. Consequently, the transition to lead-free solder does not affect the "stability" of the interconnected metal production system for all but the bismuth-based solders: Shifts in resource consumption patterns occur, but overall no shortages of intermediates result. Rather the surplus of intermediates, which is disposed of, is reduced, leading to higher overall metal recovery efficiencies, and less impact per unit of metal produced since the intermediates are used and not disposed of. Figure

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[6] Note: SnAgCu is generally perceived as the most promising substitute alloy. Because the composition of SnAgCu in the table is patented, the Japanese use SnAg3Cu0.5 and the European and Americans use SnAg4Cu0.7

5.13 (see also Figure 3.13) shows the base situation in 2000, Table 5.4 shows the relative raw materials consumption, and metal and intermediate production values in percentages after lead substitution compared to the base situation in for a number of metals. These illustrate that changes in the metal production circuits are important to consider, particularly if lead is substituted by bismuth and/or silver.

Table 5.4: Relative raw materials consumption, and metal and intermediate production values in percentages compared to the equilibrium situation in Figure 3.13 for a number of metals, resulting from the introduction of the lead free solders considered. (Legends: no shading= consumed; grey shading= produced)

Metal	Raw materials	Solders investigated				
		SnAgCu	SnAgSbBi	SnZnBi	SnZn	SnCu
Pb	Primary	98	98	98	98	98
	Secondary	99	99	99	99	99
	Zinc int.	94	94	94	94	94
	Lead	98	98	98	98	98
Sn	Primary	126	123	113	123	128
	Secondary	168	162	134	160	177
	Tin	130	127	115	126	133
Cu	Primary	100	-	-	-	100
	Nickel int.	100	-	-	-	100
	Secondary	100	-	-	-	100
	Copper	100	-	-	-	100
	Copper int.	100	-	-	-	100
Bi	Kroll B.	-	336	462	-	-
	Anode S.	-	259	453	-	-
	Special R.	-	640	3939	-	-
	Other	-	529	3254	-	-
	Bismuth	-	387	1191	-	-
Zn	Primary	-	-	100	100	-
	Iron int.	-	-	100	100	-
	Secondary	-	-	100	100	-
	Zinc	-	-	100	100	-
	Lead int.	-	-	94	94	-
Ag	Parkes C.	159	115	-	-	-
	Anode S.	159	115	-	-	-
	Primary	159	115	-	-	-
	Gold int.	93	98	-	-	-
	Secondary	110	103	-	-	-
	Silver	141	111	-	-	-
	Silver int.	152	113	-	-	-

In the base situation (2000) the by-products of gold and lead production form a considerable source of the raw materials for silver. There is no (gold) or a small (in the case of lead, from the Parkes process) surplus of the by-product that can be used in case of higher demands. As a result, the growth in the demand for silver (141%) due to transition to a tin-silver-copper solder can not (holding all other factors constant) be matched by a greater supply of the gold

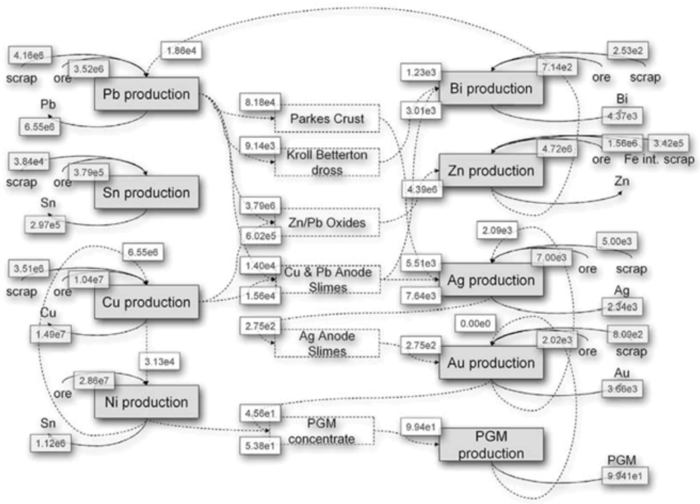

Figure 5.13: Simplified representation of the mass flows in the interconnected production system of eleven metals. The mass flows are given in tons metal/a.

(93%) and must be compensated for by greater consumption of lead (159%) intermediate and ore (159%). This means that the raw material mix per unit silver produced changes, and the demand for copper and lead anode slimes, and silver ores increases. The increase of silver in electronic scrap leads to an increased recovery as copper anode slimes (134%).

For bismuth (Figure 5.14) the situation is even more pronounced as bismuth has no dedicated ores, and lead production processes are the main sources of raw materials for bismuth. Figure 5.14 shows the effects on the metal production system for the SnZnBi solder: the demand for lead decreases (to ≈ 99%), while demand for zinc slight increases with a tenth of a percent, tin (115%) and bismuth (1191%) increases. As a consequence, the figure shows a significant impact on the supply and consumption (and thus disposal) of intermediates, and on the production routes of bismuth and tin. The present surplus of bismuth intermediates is reduced, because its supply from lead production dwindles, while bismuth production and demand for intermediates increase. As the lead intermediates (Kroll Betterton dross and anode slimes) are prime feedstock for bismuth producers, its decreased availability forces bismuth producers to look for, and switch to alternate feedstock. In the base situation (2000) only a small portion of the bismuth production comes from other intermediates (represented by resources from special refinery and other processes in Figure 5.14) in proportion to the lead intermediates, and it is doubtful whether sufficient of these intermediates are available to enable a full transition to SnZnBi-solders.

Thus, new intermediates from the production of other metals must be found, for example from tin production (see the metal wheel in Chapter 2). This example shows a paradox: bismuth is to replace lead in solder, but lead is its source. In the model, this paradox is solved by assuming that new resources for bismuth can be found. If bismuth is produced from intermediates, effect on resources depletion will be minimal, obviously dependent on the efficiency of these alternative production routes.

Another problem of the paradox is that an increased content of bismuth in electronic scrap may lead to problems in copper processing and thus for the recycling of the solders [263]. The copper smelters produce high purity copper cathodes, but some of the bismuth in the feed follows the copper smelt and contaminates the cathodes. Since the European smelters - the Boliden, Noranda and Norddeutsche Affinerie smelters - currently, with the exception for Umicore, have no possibility to separate the bismuth from the cathodes[7], the use of bismuth-containing solders could result in the situation that the smelters can no longer recycle the electronic scrap. In this study, the two alloys containing bismuth could cause significant problems. The metal wheel shows that metallurgical expertise and capacity is available to recover the bismuth from electronic scrap in copper processes. Metallurgically, lead and bismuth are similar metals. Umicore has a lead smelter, and can therefore separate the bismuth downstream of the copper furnace. As discussed above, bismuth is separated during lead refining. Thus, by attuning the copper process so that bismuth reports to the lead slag, bismuth can be recovered. Bismuth follows lead in the lead slag processing and is recovered in the Kroll Betterton dross. Paradoxically, lead processes may prove necessary for recycling of metals from lead-free solders.

5.4.3 Product designer and manufacturer

Designers and manufacturers have to solve some obstacles to produce lead-free solder based electronics, including costs, resource availability, energy consumption, and the characteristics

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[7] Today, the smelters are keeping the bismuth content of the feed within operating parameters by sampling the wasted electric and electronic equipment. If the bismuth content is above a certain level, the smelters impose penalty fees that the suppliers have to pay.

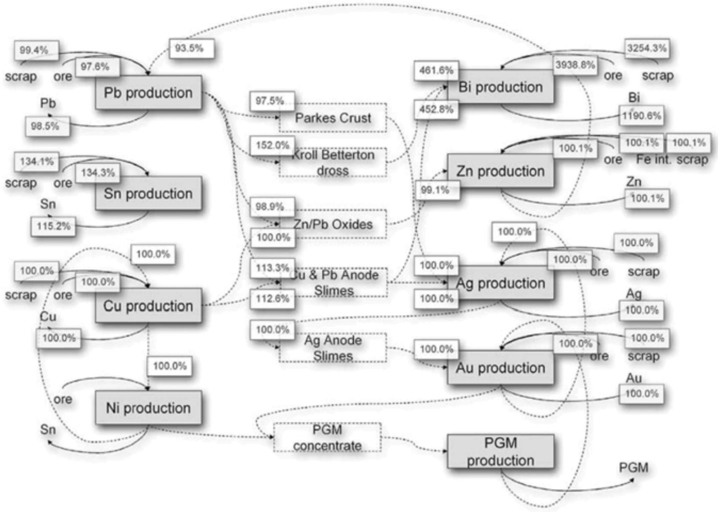

Figure 5.14: Transition to SnZnBi solder - relative mass flows in the global metals compared to the base situation are given in percentages

of the substitute solders such as processing temperature, and reliability. Much of the research efforts have focused on a direct replacement for the mainstream (63/37 or 60/40) tin-lead alloys; possible candidates should at least have comparable characteristics. The effects of the generally higher melting temperatures and other solder characteristics on the reliability of the soldering or on the soldering process are not included in the case study. In comparison to the wide range of investigations on the characteristics of alternative solders, other problems such as environmental impacts, resource depletion and energy consumption received little attention [264]. Because of the focus on the metal resource cycles - rather than on solder life cycle as common in life cycle analysis of products (LCA, see Chapter 2) - the energy consumption in the manufacture of electronics is not included in the study, nor the energy use during consumption of these appliances. Rather this case study is meant to feed the ongoing discussion whether lead free solders improve the environmental performance of electronic products (see e.g. Fishbein [258], Deubzer et al. [265, 264], Hamano et al. [266] and Turbini et al. [267, 268]). As mentioned in Chapter 3, the interconnections of industrial processes are often not or only partly considered in LCA. However, due to the complexity and non-linearity of the metal production system, a neglect of these interdependencies may lead to considerable errors in the LCA results. To investigate the effect of interdependency on environmental impact, the endpoint or damage-oriented Eco-Indicator '99 method is used [269]. The method aggregates the different emissions, and calculates the damages the environmental emissions cause to human health, ecosystem quality and resources, using damage functions. The damage functions represent the relation between the impact and the damage to human health or to the ecosystem. The method expresses the damages the environmental emissions cause to human health, ecosystem quality and resources in Eco-indicator points (Pt) . In the damage function of human health, these points represent the number of year life lost and the number of years lived disabled. In the damage function of the ecosystem quality, they represent the loss of species over a certain area during a certain time, and in the damage function of resources the surplus energy needed for future extractions of minerals and fossil fuels (surplus energy method). Although the weighting of the three impact categories into a single score allows easy interpretation, it is also the most critical and controversial step in the methodology. Therefore, both the aggregated score, as well as the individual damages will be used in the evaluation of environmental impacts.

As an estimate of the impact of the introduction of lead-free solder, the difference between the base lead-tin scenario and the lead free scenarios is used. Figure 5.15 shows the difference between the base scenario and the lead-free solder scenarios. The X-axis displays the different solders scenarios. The Y-axis gives the relative impact of the scenarios, as a single score (Total) and subdivided into damages to resource reserves (Resource Depletion, RD), ecosystem quality (EQ), and human health (HH). A positive number for any of these damages means increased environmental consequences while a negative number means improvement.

The results indicate that the Eco-indicator '99 LCA scores for a number of lead-free solders are higher than for the conventional solder. This is partly due to the higher environmental impact of tin resource depletion compared to lead resource depletion: All solders have higher tin concentrations. The silver containing solders have lower impacts, due to the interconnections between silver and gold production: In silver production intermediates are produced that serve as raw materials for gold production (Figure 5.16). An increase in silver production leads to an increase in gold intermediate (152% for SnAgCu) and thus to a reduction of the amount of gold ore that is required, but also to a reduction of silver intermediate produced in gold production (93%). Because gold is a scarce metal and its stocks are highly valued in the EI-method (expressed as a high value of gold ore for resource depletion), this leads to lower resource depletion values. Changes in the metallurgical system can thus affect the

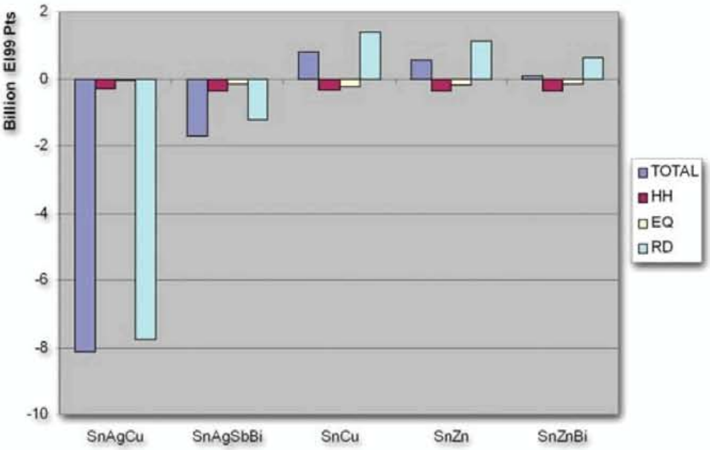

Figure 5.15: Standard Eco-Indicator '99 scores for substitution of conventional by lead-free solders

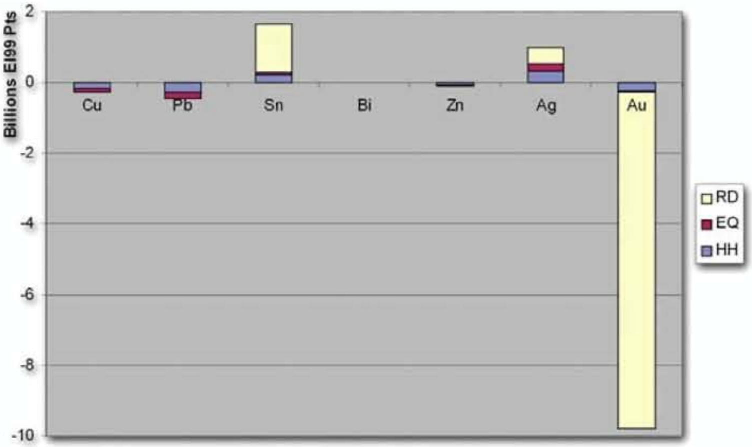

Figure 5.16: The impact of the SnAgCu solder on different metal resource cycles (determined using mass allocation)

availability of metals, and therefore the economics and feasibility of lead-free solders. Despite the higher costs of the alternatives, switching to lead-free solder will not increase the cost of printed wiring boards, because solder accounts for such a small percentage of total costs (e.g. the Ideals report [262], Deubzer et al. [264]). In general the availability of metals for solders appears difficult to estimate[8]. To estimate availabilities often the resource reserves are used (e.g. Turbini et al. [267, 268] Deubzer et al. [264]). The US geological survey defines a "reserve base" as that part of an identified resource - a resource of which location, grade, quality, and quantity are known or estimated from specific geologic evidence - that meets specified minimum physical and chemical criteria related to current mining and production practices, including those for grade, quality, thickness, and depth [227]. The term "reserves" need not signify that sufficient extraction facilities are in place and operative to meet the demand for the metals. Figures on production and production capacity are therefore required to estimate the availability of the various metals. Turbini et al. [267] use the global mining of silver in addition to the reserve base to indicate the availability of silver. In the manual on lead-free solder, the German electrical and electronic manufacturers [270] base their estimates on the difference between current production capacity and current production levels, the difference being the availability of the metals for lead free solders. The effect of lead substitution on the configuration of the interconnected metal production system, which at least partly determines whether this capacity can be exploited, was not considered in these estimates. However, switching to silver solders could consume 6 to 9% of the world's total output of silver, putting pressure on silver supplies. Deubzer et al. [265] recommended the use of silver but emphasized the need for high rates of take-back and recycling. The recommendation did not address what rates of take-back and recycling would be sufficient to ensure the availability of silver for the use in lead free solders. The simulation results show that a substitution by SnAgCu would increase silver ore consumption by more than 9% as reported in the literature, and that recycling must increase significantly to counter this effect. Based on this analysis, bismuth production can increase to 453% without changes in the raw materials consumption pattern[9]. This corresponds to a Bi percentage of 15% in the substitute solders, or a substitution of conventional solders by SnZnBi or SnAgSbBi alloys of respectively 32% or 55% (holding all other factors constant).

5.4.4 Waste manager

The EU directives require in addition to constraints to the composition of wasted electric and electronic equipment, also minimum levels of recovery. The elimination of lead from electronics products can increase their recycling value: lead is a major contaminant where substitutes such as silver have considerable value [265, 267]. Turbini et al. [267] even argued that the focus of future regulation should be on the recovery and recycling of the solder ("containment") rather than on the elimination of lead-based solder. In this process, the higher costs of the lead-free solders can provide an incentive for increased recycling of the electric and electronic scrap, and reduce recycling costs. The recycling of the metals is only partly determined by the waste processes: metallurgical processes perform the actual recycling. Generally, non-ferrous fraction resulting from treatment of the WEEE is processed in copper smelters. The metal wheel (in Chapter 3) shows that metallurgical knowledge and capacity is available to recover

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[8] For instance, the maximum contents of bismuth reported in literature range widely: In the ZWEI report a maximum content 5-7 wt% bismuth is estimated. Bi can be characterized as a rare metal, and reported a maximum content of 15 wt% in solders. Other reports estimate that the Bi supply is enough for tin-bismuth solders containing as much as 58 wt% bismuth.

[9] Note that this percentage is even lower (viz. 7%) for the SnAgSbBi solder, because anode slimes are also consumed by the silver production processes.

all the metals from the lead-free solders through the copper production circuit. Obviously copper does not present problems. Neither is the recycling of silver a problem since the increased value of the scrap can counter the potentially higher cost of recycling. Because all the lead-free solders investigated contain higher contents of tin, recycling of electronic scrap may present problems in terms of emissions due to its high volatility, or in terms of the market for the captured flue dust that contain high amounts of tin. Due to the low current yields of tin in solders, there is no substantial concern about the presence of tin. Bismuth can also be recycled in copper processes, but this will require some modifications if the bismuth levels are too high (see Section 5.4.2).

5.4.5 Policy-maker and Legislator

The potential risk for pollution of groundwater by the lead present in landfills led to the development of the directive on lead substitution in consumer electronics. However, the simulations show that related human health toxicity hazard is not dominant in the LCA scores. Rather, the LCA scores indicate that resource depletion mostly determines environmental impact of lead substitution. This is a remarkable observation, which raises the question of how to compare one environmental problem (human health toxicity) to another (damage to resources). As argued in Chapter 3, Life Cycle Analysis is a methodology, which is partially based on scientifically backed methods, but also contains subjective steps. If the final weighting step was carried out using different weighting factors, human health toxicity hazard may have been more prominent in the outcomes, and results may be different. It is often the perception of the relative importance of the different environmental problems or damages that in the end determines the environmental performance, or ranking of alternatives. Figure 5.15 and Figure 5.16 show, that the eco-indictor scores are dominated by resource depletion. For the above impact assessment, the Hierarchical weighting perspective is used, which weights human health, ecosystem quality and resource depletion damages as 30:40:30. Sometimes, however, resource depletion is considered more of an economical than environmental problem. Moreover, the uncertainty in the "surplus energy method" used in the Eco-Indicator '99 may lead to overestimation of the mineral depletion values in particular for gold and nickel [271, 272, 273]. Huisman [273] therefore suggested to reduce the weighting of resource depletion in the Eco-Indicator method from 30% to 5%, or not to consider resource depletion at all (the remainder being divided between damages to human health and ecosystem quality). If resource depletion is not considered, than all lead-free solders scenarios show a reduced environmental impact, more or less in the same order of magnitude; the silver containing solders score worst, and the tin-copper solder scores best. If the weighting of resource depletion is reduced to 5%, all lead-free solders score better than conventional solders. The silver containing alloys score better than the other lead-free alternatives. The impact of the three other solders is in the same order of magnitude, the SnZnBi alloy having the lowest impact. This points to the fact that quantitative models of the metal production/recycling system would benefit from a general value system for weighting different damages, in addition to a further convergence in the different impact assessment mechanisms. Consensus on environmental impact arising from emissions and extractions would improve the capacity to link different efforts on product design, process improvement and legislative and policy instruments in a meaningful way to the impact on the environment and to each other.

Independent of the environmental impact of resource depletion, the effects on resource availability are important to consider for legislators and policy-makers. The simulations show that because of the life spans of electronics, and the model dynamics, it takes more than three decennia before the model reaches a new steady-state. Secondary materials only become

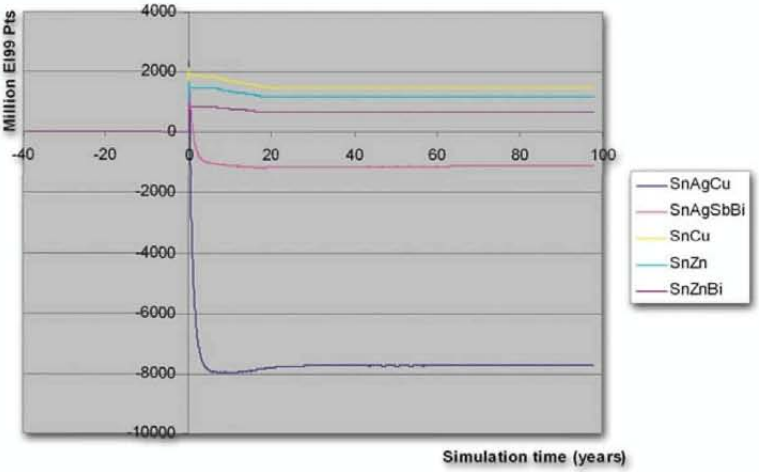

Figure 5.17: Resource depletion scores (Eco-Indicator'99) of the different scenarios as a function of simulation time in years

available after some time, and partially replace the demand for other intermediates. On the one hand this means that the temporarily shortages of intermediates for silver and bismuth can be more serious than can be expected based on the end (equilibrium) situation alone (or vice versa), due the long residence time of the metals in the consumption phase. This is reflected in the impact assessment pattern of the simulation (Figure 5.17): Overall, the slow increase in secondary materials due to higher production volumes of the lead-free solder metals result in lower impact. For the silver containing solder alloys, another effect is important: In case of substitution with the SnAgCu solder for example about 34% more silver from scrap becomes available. As this has a lower gold content than silver ore, and consequently less gold is collected in the anode slimes in silver refining process. This effect partly counters the decrease in impacts due to increased recycling. On the other hand, this also implies that problems with the availability of resources can be minimized by gradual implementation of lead free solders combined with effective recycling of its constituents. The effective recycling of bismuth and tin in solders can be become problematic. The use of these materials in the alternative solder alloys could therefore require additional policy and legislative actions. The use of tin and bismuth in lead-free solders may run into problems with the availability of raw materials (bismuth), but may also inhibit recycling of the electronic scrap in copper processes (tin and bismuth). If more than 15% of lead is substituted, new raw materials for bismuth must be found, which may require significant changes in the metallurgical processes delivering these raw materials. As a consequence, lead-free solders may only be gradually introduced; over time bismuth may become available through recycling of electronic scrap in copper processes. In copper smelters, bismuth contaminates the product, and in copper refining processes, only a limited amount can be separated in the anode slimes. At the level of copper smelters, the use of bismuth would entail a change in the operating conditions and process control to make bismuth report to the lead slag, as well as adjustment of lead production processes to accept the extra slag. Adaptation of the copper smelters to deal with elevated bismuth levels is costly. According to Umicore, owning an adapted copper smelter, bismuth is more costly to recover then its intrinsic value can justify and should therefore be avoided [263]. It requires economic incentives to make sure that the smelters will actually continue to process wasted electric and electronic equipment as stipulated in the EU directives.

5.5 Containment strategy - Cleaner recycling

Toxicity is the main driver for lead elimination. For a number of lead-containing products, a better end-of-life management of products could reduce the toxicity hazards as well. In addition, Schoenung et. al. [274] argue that recycling policies and different waste management practices are more cost effective than the EU (RoHS) directive. Although lead is a known toxicant, the alternative solder metals also present a variety of environmental impacts, especially when the entire life cycle is considered. For many of the alternative materials, data on environmental fate and regulatory standards are not available; silver appears to be of particular concern [275]. In addition, the replacement materials may also lead to higher resource depletion values (silver, copper and tin). From a metallurgical point of view, lead is an essential metal that enables an economical and environmentally sound production and recovery of a number of other metals. A phase out of lead can have a dramatic affect on the recovery potential of the metallurgical infrastructure, and on the supply of raw materials for, among others, silver, bismuth, copper and zinc. The investigation of lead free solders above already pointed out that substitution of lead by bismuth and tin could be problematic if no alternative sources for bismuth can be found, as lead is the main supplier of the raw materials for bismuth, and is also important for its recycling. As many uses of lead are (in theory at least) recyclable uses, industrial ecology suggests that the goal of lead management can also be containment instead of phase-out.

A study on lead batteries showed two complementary implications for what they call "clean recycling". First, unless primary production is dirtier than secondary production, secondary production should be the principal focus of clean recycling. Second, a clean recycling system can be achieved only if both primary and secondary smelters meet stringent environmental standards. The first implication points to lead mining and disposal as major environmental concerns; increased recycling avoids disposal and mining and thus reduces leaks from the industrial system. The recycling and primary production processes are both a source of environmental concern, because in both cases largely the same equipment is used. Except for mining processes, primary and secondary lead (and zinc) concentrates are smelted to lead bullion and subsequently refined to produce lead metal in the same processes. The overlap in primary and secondary lead smelting routes is schematically depicted in Figure 5.18. Secondary lead resources - apart from the recycling of lead from obsolete lead-acid batteries, which is carried out in dedicated processes - are typically smelted in the KIVCET, the QSL and the Kaldo processes along with the primary concentrates. Ore concentrates but also secondary materials containing zinc are processed in the ISF, which produces lead bullion and impure zinc and cadmium, which are further refined in zinc processes. The blast furnace also accepts some secondary lead raw materials. Thus, production of lead from secondary resources is no dirtier than from primary resources, as both are mostly carried out in the same processes; the main differences between the two routes are mainly the mining and ore concentration processes.

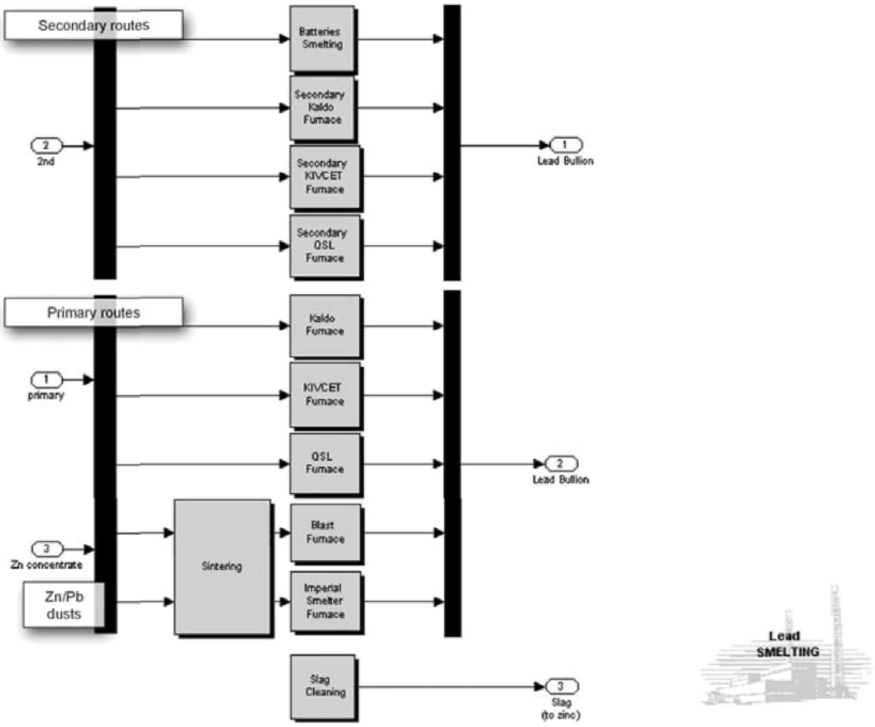

Figure 5.18: Primary and secondary lead smelting routes in Simulink™

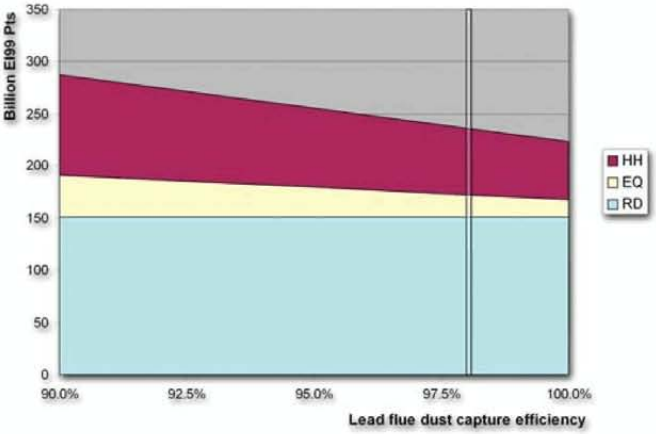

Figure 5.19: The effect of different lead flue dust capture efficiencies on the Eco-Indicator '99 scores of the interconnected metal production system. The highlighted represents a five percent increase in flue dust capture

5.5.1 Policy-maker and legislator

To promote clean recycling, legislators and policy-makers have to enable the reduction of environmental impact of lead processes. To reduce process emissions, there are basically two options: further increase the (end-of-pipe) off-gas treatment or stimulate new technology and phase-out old. Investigations of the interconnected metal cycles by Scholte [150] showed that in particular the efficiency of flue dust capture has a strong influence on the total environmental impact, expressed as Eco-Indicator '99. The effect of a five per cent increase in capture efficiency on the Eco-Indicator '99 scores is shown in Figure 5.19.

Over past decades lead production processes in the Western world have installed more and more advanced off gas treatment, which reduced emission significantly (see e.g. Nriagu and Pacyna [209], Pacyna [276], TNO [277], and Thornton et al. [222]). Outside the western world, control measures are not always enforced to the same degree and still leave a considerable margin for improvement particularly in Asia and South America [278, 210]. It should be emphasized that the metallurgical system operates at a global scale. A large amount of "Western" scrap is processed in developing countries for instance. A reduction of the environmental impact of lead use would be most effective if targeted at the countries with the largest margin for improvement: Investment in the developing countries, rather than improving the already advanced facilities in the Western world. In addition, it was argued in the previous chapter that applying too strict environmental standards, without proper consideration of the function of the process in the industrial network, may render some critical recycling processes unprofitable.

Traditionally, lead is smelted in a blast furnace (BF) or the imperial smelter furnace (ISF). These two-stage processes (sintering-smelting) have higher risks for hazardous dust and fume to be released, than the direct smelting processes. This necessitates the use of extensive and expensive exhaust ventilation. This than would lead to large volumes of lead-laden exhaust

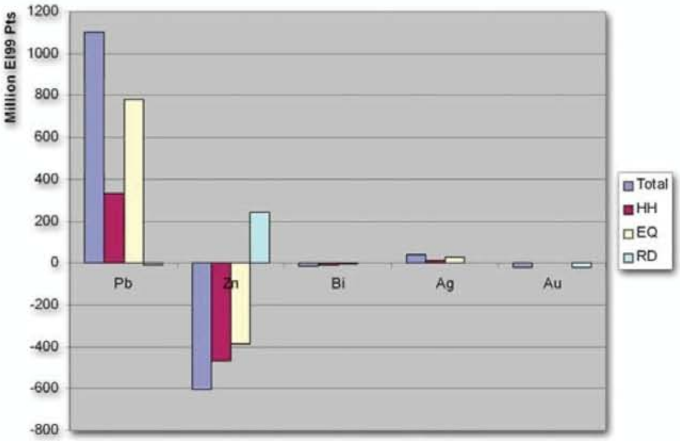

Figure 5.20: The effect of a phase-out of sintering-based lead processes on the Eco-Indicator '99 scores for the interconnected metal resource cycles, and for the lead, zinc, bismuth, silver and gold cycles individually

gases, which must be cleaned before they can be discharged into the atmosphere. Over recent years five of the world's twelve ISF smelters have closed or were converted to accept alternative raw materials [279, 227]. Modern smelting operations have therefore been developed that apply direct melting operations and avoid the sintering operation. The KIVCET, the QSL and the Kaldo processes are the most abundant examples of the new processes.

Simulation of the phase-out of the two-stage processes shows that this leads to reduced emissions of carbon dioxide, nitrous oxide and sulphur dioxide, as well as to a decrease of the total amount of flue dust. In contrast to what may be expected, a phase-out of sintering processes leads to an overall increase in environmental impact. The combined environmental burden of the lead and zinc production alternatives (direct smelting process and hydrometallurgical zinc process respectively) is higher than the burden of the ISF process which simultaneously produces lead and zinc. Figure 5.20 shows that it leads to an decrease of the overall zinc impacts, and a increase of the lead impact. When the environmental burden is distributed over by lead and zinc production (based on their production volumes), the ISF has lower emissions per ton of lead produced than its direct smelting alternatives. Per ton zinc production, phase-out of the ISF leads to a decrease of environmental burden, even when part of the burden of ISF is allocated to lead. This is because emissions to air in the Eco-Indicator method lead to higher impacts, than impact to soil and water from residue disposal and the hydrometallurgical generates less emissions to air, but more to soil and water. Figure 5.20 also shows that the phase-out leads to a small increase in lead production efficiency and a decrease of zinc production efficiency. The hydrometallurgical zinc production has a smaller capacity to process lead-zinc concentrates, complex flue dusts and residues. Some of these complex resources can currently only be refined at plants employing the increasingly rare ISF extraction process. In the model, complex zinc and lead concentrates and residues, such as EAF dust, copper flue dust, hydrometallurgical residues or pyrometallurgical slags from lead smelters, are first processed in the slag-fuming process or in the Waelz Kiln. Part of the Waelz oxide is directly sold as product (20%), the remainder is further refined together with slag-fuming product in the lead blast furnace process, the ISF process and the hydrometallurgical zinc process. The simulated phase-out leads to change in the recycling routes for complex zinc and lead resources. Without these processes, the Waelz oxide arising from the recycling of secondary resources with a low zinc and lead content must be treated in the hydrometallurgical zinc process. This partly counters the increase the efficiency of lead production arising from the use of the advanced direct-smelting processes. The lead production efficiency of the interconnected metal production system decreases because the zinc hydro-metallurgical route can process the Waelz oxide[10] but does not produce lead (a small decrease in resource depletion in Figure 5.20). The phase out of ISF processes may lead to problems for processing of certain ore types. In the simulation, therefore, also the average composition of the zinc and lead ores processed changes. For zinc production, the phase out of the ISF leads to a small decrease in zinc production efficiency due to a decreased efficiency of the recovery of zinc in lead concentrates (an increase in resource depletion in Figure 5.20). As can be expected, emission reduction leads to substantial improvement of the environmental performance of lead production. The improvement of the system through phase-out of old technology, however, is less obvious due to the interdependency of metallurgical processes. This illustrates the need for understanding the metallurgical network in order to control it. The changes in the composition of the feedstock of the reactors have a significant impact products, intermediates and residues/emissions - and thus on the performance of the metallurgical network as a whole - that are difficult to predict with the linear models of the process steps. One should thus be careful to draw conclusions form the simulation results whether of the phase-out of old technology is an improvement or not, but the results are an excellent starting point for discussion with industry the role of old technology in metallurgical production network, and improvement to the model.

5.5.2 Waste manager

The principal focus of clean recycling is stimulating the use of secondary resources. This also implies considering the chemical and physical composition of these secondary materials. Lead is an important carrier metal for the recycling of a number of other metals, such as copper, arsenic, silver, cadmium and bismuth. These metals are concentrated in intermediates and by-products, which enables the refining to recover the pure metals. In the recycling process in addition to lead, thus a number of other valuable metals are produced. If additional materials are collected and pre-treated to increase lead recycling, waste managers need to consider this: Which metals can be recycled, and which metals (and other impurities) results in problems for the downstream recycling? Is separation necessary, and do the current pre-treatment and separation processes collect the co-recyclable metals in the "right" fraction? Moreover, because of this overlap and the interdependence between the production routes of metals, changes in the recycling of lead also affect production of other metals. To investigate the effect of increased recycling on the metallurgical system, a ten per cent increase in old lead scrap recovery is stepwise introduced, which reduces the environmental pressure from waste disposal to the same extent. A problem for simulation of increased recycling is estimating the composition of the extra old scrap recovered, and the waste fraction in which it reports to the metallurgical processes[11]. Because of the difficulty of providing reliable estimates of the

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[10] See the appendices for a full description of the production routes of zinc and lead.

[11] In general, the law of the diminishing returns would suggest that it would be increasingly difficult to recover more lead at the same or higher composition or grade. This relation between grade and recovery is also observed in mineral separation processes in industry [280, 281] and can also be used to describe separation

composition. it is assumed that only lead recovery increases while the recovery of all other metals remains constant. It can be seen easily that this would slightly reduce the concentration of the co-elements in the old lead scrap, while their absolute recovery remains constant.

5.5.3 Metallurgist

Increased recycling leads to a smaller demand for lead ore concentrates and to a change in the utilization of the different lead smelters. Consequently, it reduces the emissions of sulphur dioxide, carbon dioxide, nitrous oxides and flue dusts from the lead resource cycle. Moreover, the total emissions of lead into the environment are reduced. Thus, as can be expected, the environmental impact of the industrial lead resource cycle is reduced. Figure 5.21 shows the change in emissions due to the increased lead recycling. Almost all emissions are reduced, excluding a few emissions to air and soil. Due to the decreased lead disposal on landfills, lead emissions to soil and water are significantly reduced. The decrease in environmental impact may be less than expected, due to a slight increase in the emissions of lead to air, and a subtle decrease in lead production efficiency, following from the change in process routes employed. Because airborne emissions of lead are assigned a higher impact on "Ecosystem Quality" in de Eco-Indicator'99 than those to water and soil, this leads to an increase in damage to Ecosystem Quality. Figure 5.22 shows the impact of increased lead recycling on the different metal resource cycles. As more lead is produced via secondary routes, the "primary" ISF route becomes less used (Figure 5.18). As mentioned before, the environmental costs of ISF operation are allocated to lead and zinc (and to a smaller degree also to the other minor metals), this leads to an increase in impact for the lead resource cycle, and a decrease for the zinc resource cycle.

The increased recycling also affects the production of other metals. Figure 5.22 shows that these effects, expressed as environmental impact, are in the same order of magnitude as the effect on the lead resource cycle itself. Primary copper concentrates are partly obtained from the processing of lead(zinc) ores. An increase in lead recycling leads to a decreased demand for in lead, and thus to decreased production of copper concentrates in processing of lead ores. As a consequence, this leads to increase in copper mining and thus to a higher environmental impact. Similarly, because secondary lead scrap contain less silver and bismuth - even when compensating for the assumptions for lead recycling above - increased lead recycling reduces their recovery in Parkes crust, Kroll Betterton dross and anode slimes. As a consequence the present surplus of these intermediates is reduced, leading decreased disposal of intermediates, higher system-wide efficiencies for silver and bismuth, and thus lower overall environmental impact. Moreover, the change in silver production indirectly also affects the gold production since silver production processes provide raw materials for gold production.

5.5.4 Product designer and manufacturer

Lead prevention is particularly important for products that can not be recycled, or are recycled to a limited extent. In the selection of the alternatives, the status-quo on toxicity of possible substitutes throughout the life-cycle of the solders must be compared to that of lead. The lead prevention and containment strategies are thus complementary, but their benefits do not simply add up.

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of wastes [51, 7]. Following this train of thought, the extra recovered lead scrap would be of a lower grade. However, the grade/recovery interdependence is determined by the chemical composition and physical structure of the disposed products, and the employed liberation and separation processes. Product consumption, waste infrastructure and waste management practice differ significantly between countries, or even regions. Thus, dependent where the lead scrap is recovered, increased lead recycling could also lead to scrap of a higher grade.

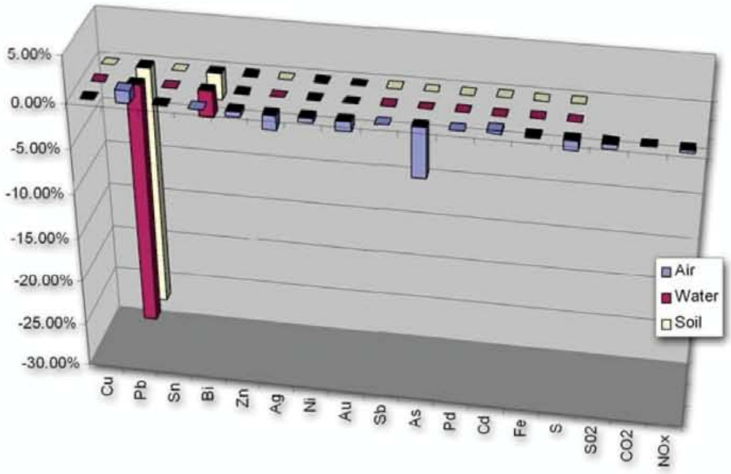

Figure 5.21: Change in emissions of the global interconnected metal cycles due to increased lead recycling

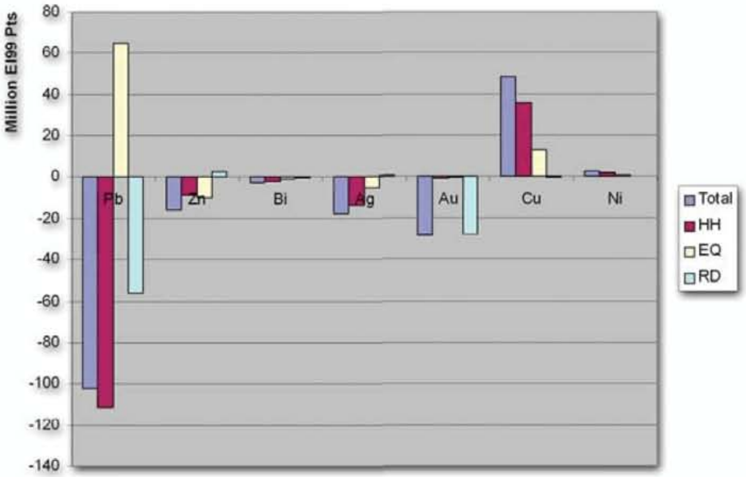

Figure 5.22: Eco-Indicator'99 score of the increase in lead recycling allocated to lead, gold, silver and zinc resource cycles

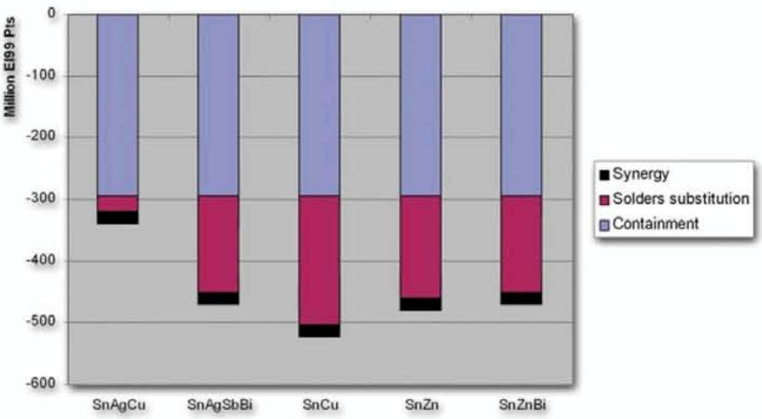

Figure 5.23: The effect of cleaner recycling on the impact of lead-free solder on Ecosystem Quality (Eco-Indicator '99)

Increased recycling affects the dynamic interdependence between the metal production circuits: the stocks or surpluses of intermediates, which act as a buffer to change in the upstream production systems, are reduced (Figure 5.22). As a result, a subsequent change in the carrier metals has a stronger effect on the production of other metals, than it would have without the increased lead recycling. Lead recycling thus may influence the environmental impact or feasibility of lead-free solders (see). To show the effect of cleaner recycling strategies on lead-free solder substitution, a cleaner recycling strategy (5% increase in flue dust capture and 10% increase in lead recycling) is combined with the substitution of lead-free solders in Table 5.3. The combination of containment with substitution of lead-solders affects the environmental impact of the lead substitution, and the availability of metals for the substitution:

- *Environmental impact*: shows three effects: the effect of cleaner recycling, the effects of lead substitution (both compared to the base situation) and the synergetic effects of the combination of both strategies. In particular because of the decrease in flue dust emissions the effects of containment are larger than the human health (HH) and ecosystem quality (EQ) effects of lead substitution. In particular flue dust capture has a large influence on environmental impact in terms of HH and EQ (see Figure 5.18). The effects of lead-free solder substitution on HH and EQ differ per solder (see also Figure 5.14). Compared to lead free solder substitution alone, these synergetic effects are significant in terms of human health and ecosystem quality[12] (the "synergy" benefits in).
- *Resource availability*: The increased recycling of lead reduces the production of bismuth

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[12] The effects on resource depletion are small (≈1%) as can be expected, but the human health and ecosystem quality of lead substitution increase by approximately 10%, except for the human ecosystem quality benefits of SnAgCu, which is almost doubled 76% increase.

and silver from the lead intermediates. As a consequence, bismuth content in lead-free solder alloys is reduced from 15% to 14%.

This illustrates that both strategies affect one another: increased recycling leads to smaller benefits for the lead-free solders in terms of human health and ecosystem quality, but to a decreased availability of bismuth. The simulation showed that lead substitution is a dynamic problem: actual benefits and availability of metals are dependent on the actual configuration of stock and flows between the different processes. This illustrates the importance of understanding the dynamics in the metallurgical system underlying the different abatement strategies for lead exposure.

5.6 Discussion

In the previous chapters, it was argued that quantitative models are essential to link different efforts, such as product design, process improvement and legislative and policy instruments, in a meaningful way to the impact and operation of the metal production/recycling system. These models must connect the dynamics at process level to the development of the global resource cycles. In this section, the model is evaluated as an example of such bottom-up construction to assist decision-making in complex, interdependent systems.

5.6.1 Linking decision-making

The efficacy of many of the IE strategies is determined by the flows, transformations and accumulations at process level. Bottom-up models, such as the one presented in this chapter, can provide for a "common ground" to discuss the implications of different strategies with industry, and can assist selecting the appropriate industrial partners to be included in the policy development process. The hierarchical method of modelling and representation provides a transparent overview of the interconnected metallurgical resource cycles, and would be suited to initiate further development of the products, or the production network by the stakeholders involved. As such, the model could assist in making the metallurgical knowledge available for waste management, formulation of policy, development of legislation, or product design and realize a more sustainable production and use of metals.

The most important contribution of the case study on lead production is that the dynamic model of the interconnected metallurgical processes allows one to investigate the impact of a shift in product composition or process configuration on the operation and environmental performance of the industrial metal metabolism. The simulations showed quantified how the interdependence in the metallurgy can affect policy-making, development of legislation or product design. This would assist co-ordinated decision-making across different organizational levels, and between processes in different resource cycle stages.

5.6.2 Capturing interdependence

Neglect of metal cycle linkages and dynamics in policy formulation or product design may lead to a shortage of lead-substitutes or errors in estimated environmental benefits. The model shows how lead substitution in solders disturbs the flows and stocks in the metal production system and that the effect of some solder compositions on the larger metal system is much greater than of other compositions, and thus their effect on the environmental impact or availability of raw materials. For some solders, the transition results in a reduction of the amount of intermediates that is disposed of, and thus in higher production efficiencies of some metals. For other solders, it can result in significant changes in consumption of energy and raw materials, and in shortage of the raw materials. The production of some lead-free solder alloy components, such as bismuth or silver, can not independently be changed: Their production is closely linked to the production of lead and copper. The simulations showed bismuth production can increase to 453% without changes in the raw materials consumption pattern or without having to find new bismuth sources. This corresponds to a Bi percentage of 15% (holding all other factors constant). The amount of change is dependent on the actual configuration of stock and flows between the different processes: The maximum percentage becomes even lower (viz. 7%) for the SnAgSbBi solder, when considering that anode slimes are also consumed by the silver production processes. The case study illustrated that the interdependence in metal processing must be considered in order to adequately estimate the environmental impact. The model can assist Lucas on metals, or metal-containing products by estimating these effects. However, the simulations show that the environmental performance of lead free solders is strongly dependent on the perception of environmental problems. The difference in these perspectives and in impacts assessment methods in general, hinders direct adoption of the results in terms of environmental impact of metals, which can drastically reduce to effort for LCA studies to include the interdependence and dynamics in the metal resource cycles, rather than the detailed inventories of the underlying flows and accumulations.

5.6.3 Closing the resource cycles, a dynamic problem

The simulations show that during the transition period metal production efficiencies, emissions and waste generated and raw materials consumption continuously change. As a result, the environmental impact of producing some metals, as well as their production/recycling capacity in the system changes. The long time periods required (approximately three decades) to achieve model convergence after lead substitution illustrated that, under these dynamic conditions, the system will virtually never be in a steady-state: It is continuously affected by new product designs, development of legislation and policy, new technology or increased recycling.

For metallurgists this means that metal processes must be capable of continuous adaptation to changes in their primary and secondary raw materials. For legislators this means that to effectively tackle "non steady-state" problems, somewhere a balance between the room for technological adaptation and innovation, and the protective constraints of legislation must be found: Too strict legislation may fix technological solutions, and hinder the processes to react adequately to external changes. In addition, it must be realized that other measures to abate lead exposure, such as increased lead recycling, also affect the configuration and thus the success of lead substitution strategies.

5.6.4 A further phase-out of lead

All of these aspects become even more important if a further phase-out of lead is considered. In case of an extended ban on lead, both the availability and recovery of a range of metals will be affected. In line with the waste prevention principle, lead substitution has become an increasingly popular approach to reduce lead emissions into the environment at the source in Europe. The proposed EU directives on electrical and electronic equipment [225] are an example of this approach. Other bans on the use of lead are in place (RoSH) , or are taking effect in the near future (e.g. in vehicles, with certain exemptions [9]). In Denmark, bans on most uses of lead compounds not covered by EU legislation, and on many uses of metallic lead are already imposed (see Section 5.1.3).

The Oslo Paris Commission recommends that lead should be further substituted where appropriate. The commission, however, adds that "a detailed investigation of the use of lead in such products, including the effectiveness and safety of proposed substitutes and an appraisal of the advantages and disadvantages of carrying out specific substitutions will need to be carried out in order to assess the practicability of phasing out lead in products" [220].

Figure 5.24 shows the possible effect of a near complete lead substitution (90%) based on status of lead alternatives [282, 283](reviewed by LDA 1992, ILZSG 1992, LDAI 2002, OCDE/GD(93)67, Nordic Council of Ministers 2003, IC Consultants Ltd 200)[13] .It can be seen flows and accumulations in interconnected metal production/recycling circuits will be drastically altered, leading to shortages in raw materials for silver and bismuth, but to an increased supply or raw materials for nickel and gold. Due to increased production of silver, the demand for gold ore may decrease with 15%. The phase-out of lead will also lead to a reduced recycling capacity for a number of metals: First, the smaller lead production automatically results in smaller co-recycling of other metals through the lead route. Second, due to the decreased lead production with considerable amount of lead still in economic stocks, lead processes will be able to select old scrap to be recycled. Old scrap that is high in impurities may be refused, and consequently these impurities are not recovered. In addition, as old scrap composition is typically not the same as ore composition, this may also lead to shortages and underscores the importance of the metallurgical understanding (e.g. the metal wheel) for product design.

5.7 Eco efficient optimization of an Isasmelter

This example demonstrates how data should be measured around a metallurgical reactor to ensure that even on this level data is correct. Furthermore, it is shown that LCA's should in future provide confidence limits right down to this level in order to remain relevant for the recycling industry. Failing to do this produces irrelevant answers, not sufficiently fundamental to be able suggest improvements to the plant. This also shows, that plants that know what they are doing will set the standard and will provide real-time LCA scores as they recycling and process scrap and post-consumer material and products. This is the level of expertise the whole industry will achieve in future.

5.7.1 Background and relevance of the copper smelting

The WEEE-legislation in Europe [284], and similar developments in North America and other parts of the world, will lead to a substantial increase in treatment and supply of end-of-life electronic equipment on a global scale. The WEEE recycling chain involves collection, dismantling, pre-processing, as well as smelting and refining. Research has shown that the

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[13] Lead substitution will affect many different metals, in particular bismuth. Bismuth is an important substitute for lead. Apart from its possible applications as lead substitute in lead-free solders, bismuth is important for lead substitution in ammunition, fishing weights, tools and anchors, and lead compounds in glazes and enamels. If bismuth were to be used in all of these applications, it would dramatically increase the demand for bismuth (as much as 25 times based on average composition of lead-free solders in Table 5.3). Silver is also important as substitute for lead in alternative batteries , bearings and solders and lead substitution could increase the demand for silver more than six fold. Copper is also important as lead substitute in a number of applications: including joints in drain and water pipes solders, balance and wheel weights, and roofing plates. However, because of the relatively large production compared to lead, only a marginal change in the demand for copper can be expected. This holds also true for iron which may be used to substitute lead in among others flashing (around chimneys, windows etc.) ammunition, bearings, lead weights (fishing tools anchors and balance weights for vehicles) plating of gasoline tanks, yacht keels, lead tubes and joints (for drain and water pipes etc.). A small increase in the demand for zinc can also be expected.

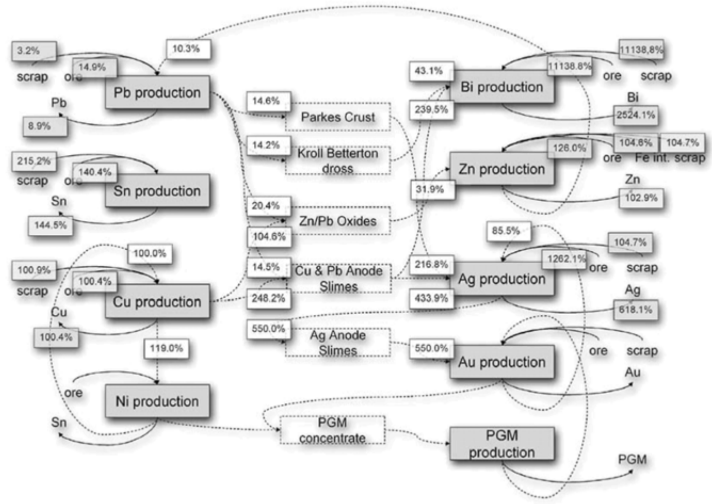


Figure 5.24: Estimated disturbance of the metal production system due to a near complete lead substitution

integrated metal recovery process has a central position in the end of life chain and that it is the key determinant in the potential realization of environmental benefits [285]. This is why the copper smelter is such an interesting example. A state-of-the-art smelter and refinery process has major impacts on the recycling efficiencies, in terms of elements that are recovered as well as in terms of overall environmental performance. Besides copper and precious metals, modern integrated smelters recover a large variety of other elements, including energy from plastics contained in the scrap. These processes close the metals cycle and form a key and integral part of the recycling chain [7]. Legislative authorities aim to minimize environmental impacts. One of their tools is the LCA. However, regular LCA practices are not sufficient to capture the fluctuations in feeds to the metallurgical reactor and cannot handle statistical based plant data. Considering industrial plant data, their fluctuations and their effect on the process chain and reactor, are required to try and answer questions on chain optimization such as: "Do real economical, environmental and ecological benefits justify all separation steps?", "How much pre-processing required before scrap can be fed into the smelter?" [286] proposed in this paper, i.e. a statistically based LCA derived from industrial plant data, can form the cornerstone in determining whether eco-efficient strategies exist. It will prove to be more suited in answering these complicated questions, through its sound metallurgical and operational perspective.

5.7.2 Umicore smelting

The Umicore smelting operation in Hoboken (refer to Figure 5.25) is able to refine a wide range of complex materials. These originate from other smelters, such as Pb or Cu matte, or simply from specific end-of-life materials such as; electronic scrap, car catalysts, industrial catalysts and burnt films. Its process is based on complex Lead-Copper-Nickel metallurgy, which offers a high degree of flexibility and efficiency that enable a maximal recovery of all metals as depicted in Figure 5.25.

The plant is one of the biggest and most advanced recycling units for precious metals in the world. It comprises of various interlinked metallurgical operations as is clear from Figure 5.25, which include the copper smelter, the leaching and electrowinning Plant, the Pb blast furnace and the Pb refinery that will all be briefly explained in the following sections.

ISASMELT copper smelter

The core of the plant is the ISASMELT copper smelter (refer to Figure 5.26). It is the input point for electronic scrap and the basis of the discussion in this paper. It forms the interface between preprocessing and metal smelting. After the copper smelter the metal loses its identity; it is impossible to distinguish from which source it came. Lead and copper matte (alloy of metal and sulphur), electrolysis slimes, electronic scrap, as well as other copper and precious metal containing materials, together with cokes make up the feed (stream 1). Diesel, air, and oxygen are injected into the furnace, and generate a turbulent bath that immerses the various components. Off gases, fumes and fly ashes are collected and treated (stream 2). The reactor's primary objective is the effective separation of copper from lead (streams 3a and 3b) and the concentration of the precious metals such as Ag, Au, Pt, Pd, Rh, Ru, Ir in the copper phase. The copper smelting process (ISASMELT) is a high temperature operation. It offers high flexibility, and hence has various types of feeds (each with their own mean and standard deviation). Sampling inside a furnace is, as in every high temperature operation, severely hindered, and operational control requires a lot of experience and insight.

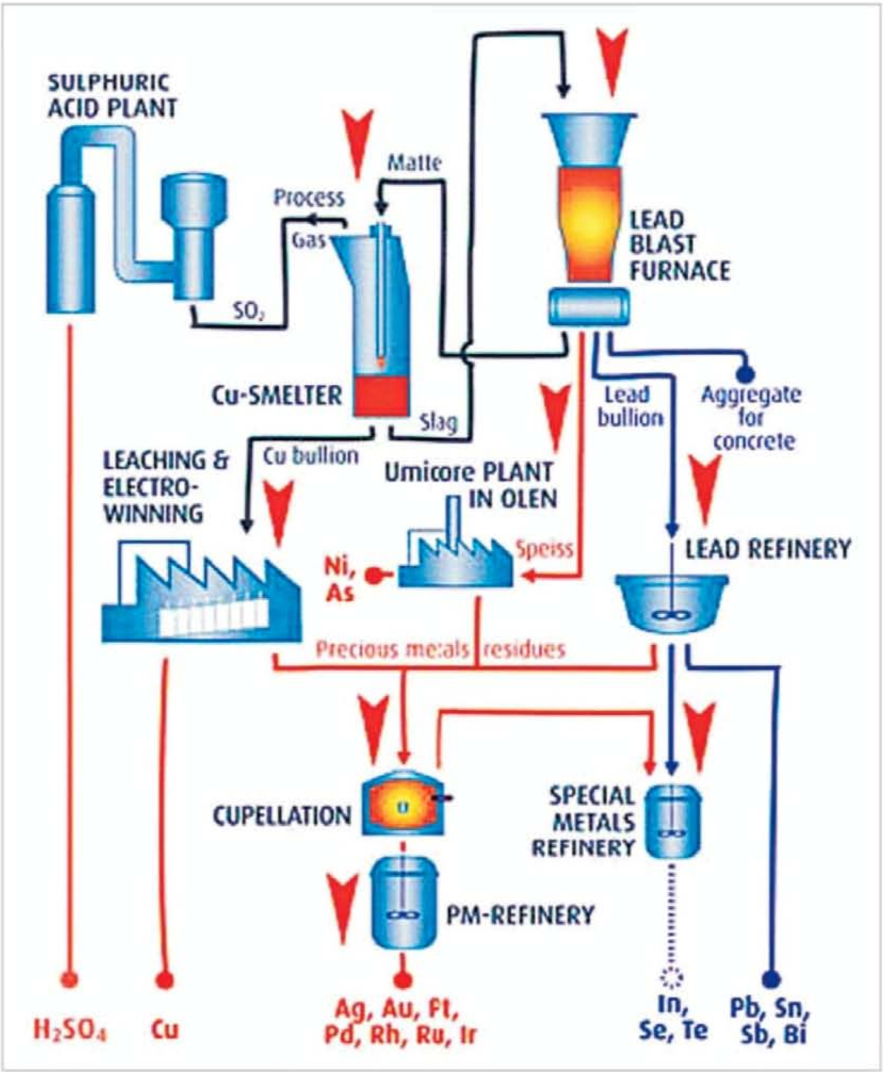
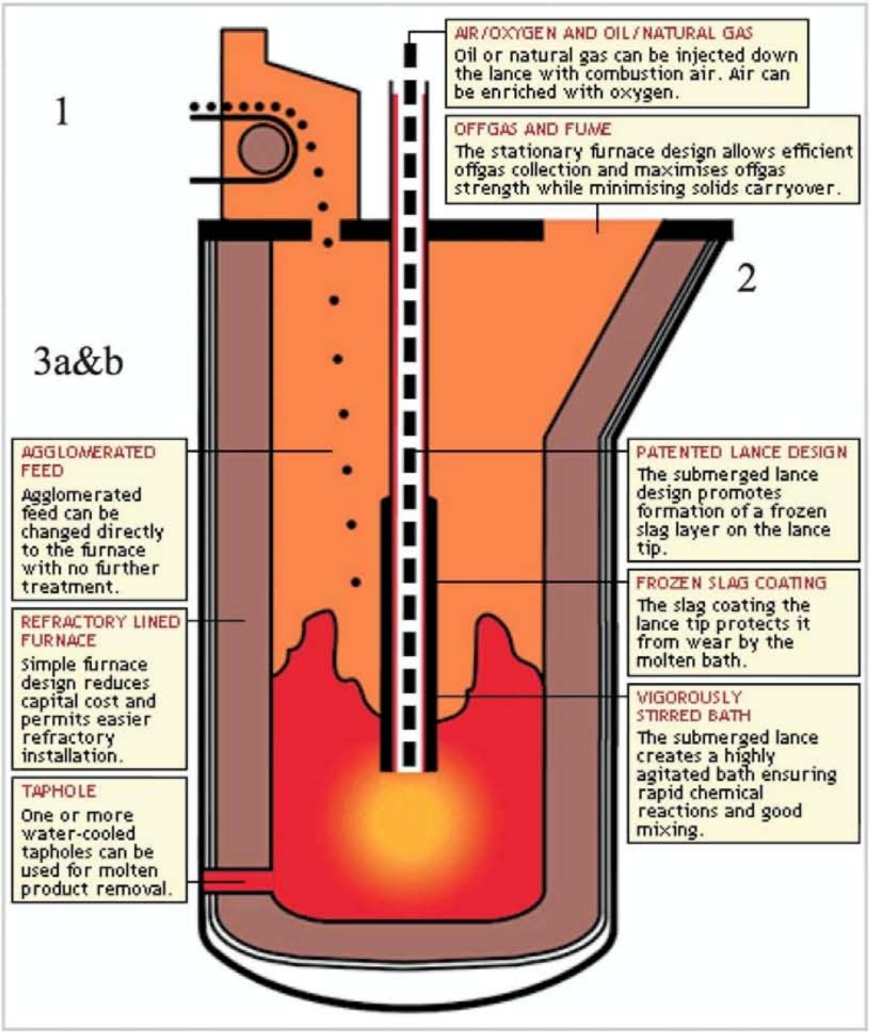


Figure 5.25: Integrated Metals Refinery (Umicore, Hoboken/Olen)



AIR/OXYGEN AND OIL/NATURAL GAS

Oil or natural gas can be injected down the lance with combustion air. Air can be enriched with oxygen.

OFFGAS AND FUME

The stationary furnace design allows efficient offgas collection and maximises offgas strength while minimising solids carryover.

AGGLOMERATED FEED

Agglomerated feed can be changed directly to the furnace with no further treatment.

PATENTED LANCE DESIGN

The submerged lance design promotes formation of a frozen slag layer on the lance tip.

FROZEN SLAG COATING

The slag coating the lance tip protects it from wear by the molten bath.

REFRACTORY LINED FURNACE

Simple furnace design reduces capital cost and permits easier refractory installation.

VIGOROUSLY STIRRED BATH

The submerged lance creates a highly agitated bath ensuring rapid chemical reactions and good mixing.

TAPHOLE

One or more water-cooled tapholes can be used for molten product removal.

Figure 5.26: ISASMELT Reactor

Leaching and electro-winning plant

After granulation, the blister copper, is sent to the the leaching and electrowinning plant. Here the Cu is recovered under the form of cathodes by electro-winning, while the precious metals are collected in the leach residue and are further refined in the precious metals refinery.

Pb blast furnace

In the Blast Furnace Pb and Pb/Cu rich materials are converted into speiss (Alloy of metal, semi metal, and sulphur), Pb bullion, copper matte and slag. The impure Pb, which among others contains Ag, Au, Pd, Sn, Sb, and Bi is sent to the Pb Refinery. The speiss which contains most of the remaining platinum group metals is sent to Olen (another Umicore plant) for further processing. The noble metals are separated and sent back to Hoboken. There copper matte is fed back into the copper smelter, and the slag is used in the construction industry.

Pb refinery

In the Pb refinery the Pb bullion is refined into pure Pb. Noble and other metals are extracted from the Pb and recovered. The Parkes-process desilverises the Pb and concentrates the noble metals into a triple alloy (Pb/Ag/Zn). Zn is subsequently removed in a vacuum induction furnace.

Precious metals refinery

The precious metals concentrates for the various upgrading processes are transformed into highly purified compounds through both hydro and pyrometallurgical processes.

5.7.3 LCA model approach

As described earlier, a general LCA approach would fail to characterize the complex interactions and fluctuations created by the various changing feeds, operational changes etc. A statistically based LCA methodology is proposed, comprising of four steps (refer to Figure 5.27). The following four steps will be addressed in the sections below.

- plant measurements,
- data reconciliation,
- model parameterisation, and
- Life Cycle Assessment (LCA) statistics.

The approach will be illustrated by following the element Ag, throughout the whole chain. Throughout these sections there will be reference of two used models. The Data Reconciliation Model refers to the model that was used to balance the plant measurements. The FEED model refers to the model that provides predictions for the various phases (e.g. blister). Both use and explanation on both of these will be provided in Sections 5.7.3 and 5.7.4. Once steps 1 to 4 have been successfully completed, step 3 and 4 can be taken out and used to determine whether opportunities for chain optimization exist. This aspect will be addressed in Section 5.7.6.

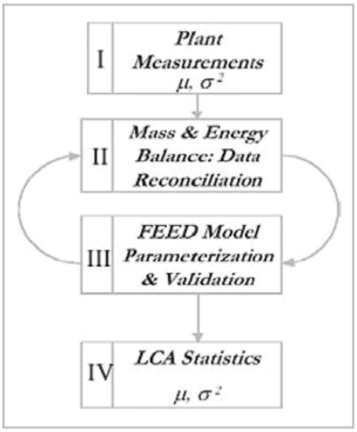


Figure 5.27: Methodology used to measure and model data

Plant measurements

Umicore has provided data of all measurable variables. The data represent a variety of feed conditions (e.g. with and without scrap). Analyses of slags, off gases, cokes, and the various input types have been provided.

Data reconciliation model

The Data Reconciliation Model modifies the plant measurements. These adapted values will in turn be verified against the predictions of the FEED Model (Section 5.7.4), and provide insight into the behaviour of the system. Process data is inherently noisy, in some cases non-existent due to difficult sampling, or requires calculation/estimation from secondary measurements (e.g. off gas compositions). It is also hindered by measurement, sampling and analysis errors. To eliminate the various discrepancies in, among others, the mass balance, data reconciliation was used. It permits the balancing of system of measured data, through a mean and a standard deviation [5]. Adjustments are made to the Umicore data set in order to meet material conservation (ΔM), data integrity and user-defined constraints. The technique is widely accepted and makes the adjustments through the minimisation of total adjustments. A total energy balance has not been constructed. Instead a ΔQ was defined, referring to the energy need of the charge. ΔQ is determined through the enthalpy input minus output. The results from the Data Reconciliation Model for Ag show that it would be erroneous to characterize the smelting operation with a mean alone (refer to Figure 5.28). Please note that these graphs have been normalised i.e. x-axis for confidentiality reasons. Their means in fact are very different. One can also see that these standard deviations propagate through the furnace, and do not level out.

5.7.4 FEED Model parameterisation and validation

The results from the Data Reconciliation Model are compared to the predicted values that are generated by the semi-empirical smelter feed model of Umicore. This model is called the FEED

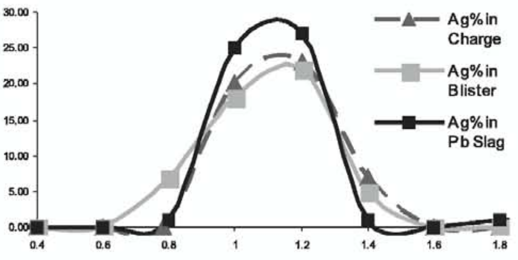


Figure 5.28: Results data reconciliation: Frequency distributions for the Ag concentration in the slag (concentration has been rendered dimensionless by dividing by average)

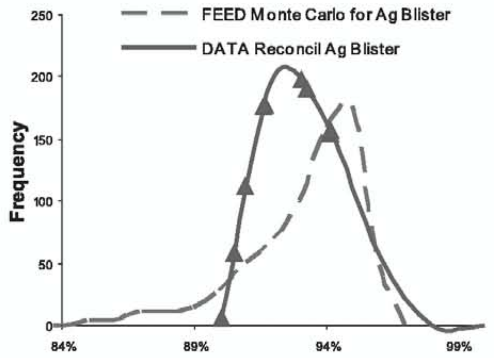


Figure 5.29: FEED Model vs. Data Reconciliation results, for the Ag distributions (concentration has been scaled to percentage)

Model from here onwards. This comparison is made to detect errors, and to validate this FEED Model. This FEED Model of the copper smelter predicts the compositions and tonnage of Pb slag, blister copper, fly ash and sulphuric acid, for a certain feed composition. It is based on a number of metallurgical principles (e.g. slag acidity), operational constraints (e.g. smelting speed, time) and mass balance constraints (e.g. split factors, or recoveries, for elements), and assumptions (e.g. %Cu in slag). A Monte Carlo simulation, that uses the results from observed standard deviations from the data reconciliation, provides insight into the propagation of variations through the FEED Model. The distributions of the assumptions within the model have been set through expert guessing. The results of the Monte Carlo simulation for one of the used feed compositions are presented in Figure 5.29. The x axis results have been normalized for confidentiality purposes. To quantify the reliability of the prediction, the (standard) coefficient of determination (R^2) is calculated for the predictions. The results have also been compared with the split factors calculated from the internal materials accounting balances of Umicore. They have been used to find and confirm model flaws, and in some cases are used for a more reliable prediction.

Please note that these annualised figures form a representation of the FEED Model. After all, the model has been used to calculate the desired feed compositions, and as such is implicitly present in the annual figures. As such, they form a representation of the behaviour of the

Table 5.5: R^2 for mass and Ag: Data Reconciliation results vs. FEED Model and annual

		Mass (%)	Ag (%)
Blister	Model	97.6	86.4
	Annual	92.9	91.5
Pb slag	Model	92.4	94.1
	Annual	89.9	92.7
Fly ashes	Model	92.5	84.5
	Annual	95.9	97.5

smelter, in concert with the rules from the model. These in turn originate from thermodynamics as well as heat and mass transfer phenomena. Once the results have been validated, the standard deviations set, and the last model adjustments have been made, one can proceed to the LCA valuation of the streams, taking into account their uncertainty and confidence level.

5.7.5 LCA statistics

The LCA can be performed on the two types of data; the predicted data set (from the FEED Model) and the real plant data (from the Data Reconciliation Model). The realized data set provides more accurate data on ΔQ, smelting time, etc. However, the predicted data from the FEED Model is more suitable for the determination of possible optimization strategies. Assigning each output stream its specific environmental impact score is a complicated issue [287]. The streams require further processing or recirculate within the plant. Various emissions are present, and can be allocated directly to the input, e.g. lead emissions to the total amount of lead taken in, such as emissions to air, water, or land. Unguided and non-specific emissions are allocated as overhead. Another issue is a feed mix issue: The amount of scrap makes up 5-10% of the total feed, depending on market prices, furnace balance etc. It is hence key to determine what impacts are dependent on the input (e.g. lower energy use) of the scrap, and which ones do not (dusting)! The specific impacts are determined through running various scenarios through the smelter model. After the ISASMELT reactor, the materials lose their character. As a result further refining (for the blister phase), and smelting emissions (Pb slag) are accounted on an overall basis. Sensitivity and uncertainty analyses mitigate some of the aspects.

5.7.6 Chain optimization

The LCA method delivers a validated FEED Model with a LCA statistic i.e. an average value and an associated standard deviation for the reactor. This in turn can be combined with a shredding and separation model [285].Adding the environmental performance for the Umicore smelter to the dismantling, and shredding and separation score, gives an insight in the overall performance. Key factors in the relation between pre-processing and metal smelting are to be investigated:

- pre-sorting of products before entering shredding and separation lines,
- optimising copper fractions for further processing: the diluting vs. losing materials, due to concentration processes issue,
- changes over time in product compositions, and

- changes over time in separation technology.

This approach then permits the evaluation statistically the following scenarios:

- analysis of sorting and direct treatment of electronic products with high to very high precious metal contents like cellular phones, DVD players etc., and
- concentrate or dilute? And what fractions to separate before they are fed to the smelter?

5.8 Summary

In the previous chapter it is shown that the current metallurgic knowledge and industrial infrastructure have the capacity to realize industrial ecology strategies, but only if the metallurgic constraints of metals production and recycling are taken into account in waste management, policy development, and product design (and vice versa). Adequate modelling and presentation of modelling results of the metal production network are required to assess the consequences of existing and new regulation, product innovations, and process improvements. The model of the interdependent industrial metal resource cycles presented meets these criteria. The model can be used to estimate the effect of regulatory, product and process changes system-wide, and identify possible bottlenecks at process level. In such a way, the model can be used to co-ordinate decision-making across the different systems levels by identifying possible (technological) bottlenecks. The system of metal production and recycling processes is too complex to fully predict the environmental consequences of technological changes or new policy and legislation. The effects of changes to the metal metabolism can not be completely modelled using mass balances only, among others due to the complex interdependence between feed composition and product quality in metallurgical processes - partly controlled by the tacit knowledge in the processes. The model can sufficiently predict system-wide changes in the system, to assist in initiating stakeholder assessments. The combined (partly tacit) knowledge of the stakeholders can be feed back into the model and further develop the model. This is why and where industrial ecologists and metallurgists must join forces. In short, metallurgical process technology know-how must complement a sound understanding of economics and regulation to bring to fruition industrial ecology concepts. Without a sound technological and scientific basis, industrial ecology will remain in theory and philosophy books.

5.9 Examples and case study

The model is useful to simulate and investigate various scenarios. The following give examples of possible situations that can be considered as examples with some hint of an answer given.

5.9.1 Decrease of copper production due to replacement of copper pipes with PVC pipes

This is a hypothetical scenario, exploring what happens to the total metal production system when the production of a base metal is greatly reduced, in this case copper. The example explores the replacement of copper pipes used in construction with some other material, for instance PVC pipes. This application of copper is ca. 16% of the total copper consumption (Copper Development Association ¡www.cda.org.uk¿). The changes relative to the base case (100%) is given by Figure 5.30. Copper is interesting to examine in that regard as it relative little direct dependent metals as the stock levels of intermediates are quite high. This is apparent when examining figure 5.7. The large decrease in copper production decrease the supply of copper anode slimes, the decrease anode slimes consumption is much lower. This is already enough to increase the lead production in order to satisfy the bismuth demand.

5.9.2 Use of different DVD players

Many products slowly evolve over the years, as functionality, durability and usage change the composition of those products change accordingly. A good example is consumer products; here the specific example of DVDs is used. DVDs are relative new products and therefore the change of product composition is relative large with each new type. In Table 5.6 the compositions of three DVD models are listed, iron and materials grouped in the "other" category are given a standard LCA value. The difference between the causal allocation and the expansion LCA score is small. Due to the very marginal changes to the demand of metals the two methods have a hardly noticeable difference. As such the easiest and quickest method, i.e. causal allocation, is better suited to examine marginal changes to the metal production system. The marginal changes to the flows in the metal production system do not warrant an extra examination and is therefore not given.

Table 5.6: The composition of three different recent types of DVD in %

DVD Type	1	2	3
Cu	7.98	4.86	5.92
Pb	0.12	0.27	0.29
Sn	0.16	0.11	0.12
Bi	0.00	0.01	0.01
Zn	3.35	0.29	0.31
Ag	0.01	0.01	0.01
Ni	0.17	0.05	0.05
Au	0.01	0.00	0.00
Fe	78.12	56.61	63.74
Other	10.09	37.78	29.54
Total weight (g)	3693	2601	2895

5.9.3 The sensitivity of the model

The following scenarios give am indication what the model can be used to investigate.

Emission of gasses

The technology used to reduce the environmental impact of making metals is different around the world. The model uses an assumption that modern technologies are used but that might not be true in the whole world due to ineffective legislation or certain inertia to build new installations. One good example is the flue dust capture efficiency. In the model it is assumed that flue dust is captured with 98% efficiency. If that efficiency however is lower the LCA-score is influenced greatly, i.e. a reduction of the efficiency by 2% to 96% increases the LCA score with increases the LCA score with 22%.

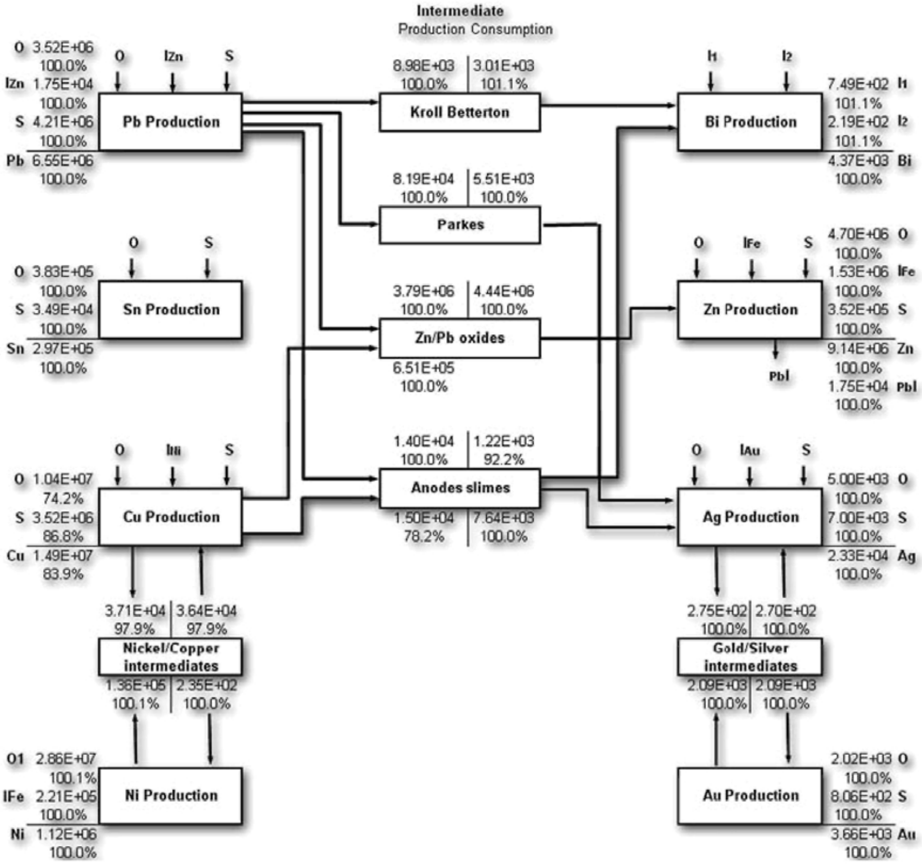


Figure 5.30: The effect of decreasing the copper production by 16% on the other connected metals *Legends: O=ore, xIy=intermediate from (y) or for (x) other metal production circuits x or y, S=old scrap. Parkes (silver removal), Kroll-Betterton (bismuth removal), Zn/Pb oxides and Anode slimes are intermediates.* 100% implies the base case and any deviation gives from this gives the change with respect to the base case.

Transportation

Between each phase in the metal life cycle the products need to be transported to another place in the world for further use or processing. The distance material travels between each phase vary for the material being transported but for mining concentrates the average transporting distance is around 4500 kilometres. Changing the average transporting distance has little effect on the LCA score.

Recycling

Recycling of metals is an important part of the metal life cycle. Recycling reduces the amount of waste produced and the amount of ore needed. In the model the metals have been categorized according to their use and for each category an estimate of their recycling rate is made. One of the categories is end of life vehicles (ELV), e.g. if in the model a recycling rate of 95% is changed to 85% the LCA score of lead would increase by 4%.

New scrap

During the production of materials out of pure metals scrap is generated that is relative pure, it only needs to be remelted before it can be used again for new product manufacturing. For zinc the model assumes that 18.8% of the zinc produced is discarded as new scrap during manufacturing and can be immediately recycled. Were this percentage decrease to 10% the LCA score of zinc would increase by 11%.

Changes to the flow sheet

The flow sheet currently implemented in the model is the flow sheet for metal production as it currently is. However, that will change as for instance technology or supply of raw materials changes. Moreover the processes itself can change; a higher recovery efficiency or a different waste material treatment.

Copper production can be used as a good example to examine what happens when the flow sheet changes. In primary copper productions there are six different methods or furnaces to go from copper concentrate to blister copper (see Appendix B). Which method or furnace is used depends on various parameters, e.g. the distribution of the copper concentrate and the availability of electricity. As these circumstances change the percentage of copper produced by each route will change.

Changing the distribution of furnaces used does not significantly affect the flows in the other parts of the metal production flow sheet, however, it does affect the LCA score of copper. The differences in LCA score are mainly caused by different flue dust and off gas emission. Using only INCO type furnaces the LCA score is 31% lower compared to using other furnaces. It is of course not very likely that in the future production will switch to only one type of furnace.

Chapter 6

Web of Metals model discussed

In the synthesis (Sections 6.1-6.4), the approach chosen and results obtained are evaluated based on the questions formulated in Chapter 1. Subsequently, important concepts, ideas and recommendations derived are summarized (Section 6.5).

6.1 Sustainability of industrial ecology

The concept of sustainability refers to continued welfare of human life on earth. It is an emerging system quality, which means that sustainability is a property of the system as a whole and that one can not know that the system is sustainable until in fact sustainability has been reached. The web of environmental processes upon which the present industrial society and thus human welfare is built, is robust with respect to perturbations, but only within distinct limits. Overstressing these limits may lead to a (partial) collapse of the natural systems, and have dire consequences for human welfare. As a consequence, sustainability of human welfare would also call for a level of "welfare" for the environmental processes. The extent to which the current consumption-based society has reached these limits or the effectiveness of measures to avoid reaching these limits is unknown. Given the expected growth in population the present definition of welfare will most likely overstress the boundaries of natural systems at some point in time. Above all, sustainability requires a redefinition of the concept of welfare. To date welfare is measured using the "having" paradigm: it is almost universally defined in terms of ability to appropriate goods and materials. An alternative definition of welfare based on "being" paradigm is necessary to ensure the sustainability of human welfare. Considering the complex dynamics of environmental processes and human activities, sustainability is probably not a specific system configuration that can be accomplished, but more of a continuous co-evolution of human and natural systems. The role of technology in this process is very ambivalent. Depending on how technology is used, it can either be part of the problem or the solution. It is therefore essential to take a critical attitude towards technology. Industrial ecology - the discipline that focuses on the sustainability of industrial activities - would appear a good analytic framework to investigate critically the role of technology and technological knowledge in achieving sustainability. The review of the concept showed that by itself implementation of the principles of industrial ecology will not lead to sustainability. Industrial ecology is an ecological or systems approach that, based on sustainable examples in nature, strives to achieve a deliberate (r)evolution of industrial activities within the boundaries set forth by natural systems they are founded on. The industrial ecology approach contains two essential elements. The descriptive element describes industrial activities in the context of other processes, both in the "technosphere" and the "biosphere". Because in the end, the industrial system interacts with nature at the physical level, the industrial activities are described in terms of flows, transformations and accumulations. The prescriptive element aims to inform the decision-makers about the (un)sustainability of industrial activities, in order to realize the desired evolution of industrial systems. The approach of industrial ecology excludes some of the basic components of sustainability. Sustainability of any of the (industrial) subsystems can not be considered without the larger systems context, whereas industrial ecology focuses on the industrial subsystem. Industrial ecology strives to be objective, not normative, and social, psychological and economic issues are evaluated as objective dimensions of the problem. These issues are critical dimensions of sustainability - they determine the perception (and distribution) of human welfare and thus the extent of the technological change required. Because industrial ecology concentrates on just a part of the problem and possible solutions, its implementation can not lead to a sustainable society. The desired evolution does provide the necessary "breathing space" to address the core issues. Moreover, industrial ecology approaches can visualize the limits of such industrial ecological evolution and thus constraint the possible definitions of welfare. While industrial ecology does not really address the question whether technology is a problem or solution, it does investigate the boundaries for industrial/technological systems that the different, possible sustainable system configurations would pose. This makes industrial ecology an essential tool for any deliberate advance towards sustainability, or investigation of the role of technological knowledge in this process.

6.2 Technological knowledge, a bottleneck for sustainability?

A deliberate evolution towards sustainability requires co-ordinated efforts of decision-makers across all system levels. Many of the top-level industrial ecology strategies require solutions at the bottom-level of technological processes. At top-level, the industrial system can be seen as a compartment in the global metabolism, in which materials are converted into products, products are accumulated and recycled into materials again. This system of resource cycles is not closed as materials leak into the environment. The resulting impact of the industrial compartment on the environment is a function of the amount of material and energy that is used in the system, and the efficiency by which they are used and recycled. This view shows two basic options to reduce the environmental impact of metals: decreased use of the amount of material/energy, and increased efficiency; both will lead to reduced impact. To investigate the strategies, the industrial metal production system is chosen. Metals are essential elements that play key roles in both the biological metabolism, and the human economies. They catalyze many processes in the metabolism of natural ecosystems, and are essential materials for human economies (industrial ecosystems) as well. The option are complementary, since even if society changes from the "having" to "being" mode metals still will be necessary in many products. The industrial metal production system constitutes a key component in the metal cycles: It performs the chemical transformations necessary to introduce or feed metals back into the material cycle. Both options require co-ordination of the different system components: The decreased use of metals in products can affect product recyclability. Which products are recyclable is determined by the development of the collection, separation and metallurgical processes downstream. The changes in the supply and composition of secondary materials resulting from product manufacturing require that metallurgical processes must be able to produce and recycle metals efficiently under continuously changing conditions. In a system of closed metal cycles, the rate of change for the individual product flows or processing components is determined by the dynamics of the slowest components. If product designs change faster than the production/recycling infrastructure can, this could result in problems with availability of raw materials from the interconnected metal production systems downstream, in a reduced efficiency of recycling, or in undesired environmental impacts in metal recycling upstream. This is the case at present, products change fast and their manufacture introduces new metal-metal and metal-non-metal combinations for which no recycling technology is available. As a consequence, recycling contaminates the produced metals. Currently, the utility of metals is maintained through addition of high amounts of clean primary (virgin) materials. On the long term, however, this would prevent closure of the material cycles. A critical obstacle for the successful implementation of industrial ecology strategies is the co-ordination of the different efforts themselves: a design for cleaner production that aims for minimum emissions and residues may as a consequence produce residues that can be further processed and not contribute closing the material cycle. The current metallurgic knowledge and industrial infrastructure have the capacity to realize industrial ecology strategies: the status quo allows the recycling of many different metals at limited environmental impacts. Because of the long life spans and development times of metallurgical processes, this capacity and knowledge can only be exploited if the metallurgic constraints of metals production and recycling are taken into account in waste management, policy development, and product design. Thus a condition for industrial strategies on metals is the proper appreciation of these constraints. The constraints are difficult to pinpoint because metals participate in a system of linked cycles and can not be produced or recycled independently from one another. Moreover, much of the operational knowledge controlling the material transformations in the processes is tacit. The concept of the metal wheel was developed to visualize the constraints and capacities in a simple manner: Based on the ore compositions for which the metallurgical system was developed, it illustrates the interconnectivity in metals processing and shows which metal combinations in products or waste fractions can be effectively recycled into metals again. The wheel indicates which impurities are recovered and which are problematic and are disposed of through process residues.

6.3 The role of models to co-ordinate decision-making

The metal wheel visualizes the capacity of metallurgical systems, but provides no information on the dynamic behaviour of the system, necessary for effective control of the system. The industrial ecological evolution aims to approach a (type III) ecosystem configuration. In nature, organisms feed and dispose of large amounts materials continuously. These organisms are bottom-up organized into ecosystems to efficiently recycle these materials. The type III ecosystems are robust in a sense that they are able to keep this efficiency under changing conditions by continuous adaptation. This adaptability is a consequence of multiple feedback loops. These tend to bring the ecosystem back into balance, whenever there is a deviation from the norm due to changing environmental conditions. Industrial ecosystems are controlled by feedback as well in a similar fashion as ecosystems. If a process becomes less economically fit for one reason or another, the technology is less likely to be reproduced in new processes and its "population" declines unless of course it is able to adapt. Because processes have distinctive material transformation functions, which often can only be partially replaced by other processes, a declining population affects the capacity of total industrial system. There are also significant differences between natural and industrial ecosystems. Perhaps most important of these is the capacity of humans to consciously plan their activities. It is this planning capacity, which in principle allows one to make the industrial system compatible and meet the needs of present and future generations and the present and future needs of the natural processes. Economics, policy and legislation translate the global environmental objectives into requirements at process level, and thus govern materialization of technological solutions and configurations. Today, much of the environmental policy and legislation is reactive: when a problem arises, measures are taken to solve or reduce it. Because of the complex web of interactions and feedback on these interactions, the effect of changes to either system may show a significant delay. Technological solutions that may appear to be sustainable may have detrimental effects on the longer run due to long delay in the feedback in the natural processes. Natural ecosystems are robust within distinct limits and it often takes time to reach these limits. This is a problem as some damages to nature are irreversible, and technological configurations may prove very difficult to alter because of the so-called technological lock-in. At process level, delay in feedback control systems is known to result in instability and thus deviation from the control parameters such as product quality or emissions. An important lesson that can be learned from ecosystems that have to deal with the same issues is feedforward control. In addition to feedback control, natural systems also exhibit feedforward control. Where feedback control is reactive, feedforward control is pro-active. As in feedforward control possible changes are measured in advance, in theory perfect control is possible: No offsets in the control parameters. The effect of these changes is anticipated based on a quantitative model of the controlled system, and is compensated for by altering the system parameters. Feedforward control could avoid the problems of feedback control, but can not compensate for non-measured disturbances or non-modelled parts of the system. Not all disturbances can be measured and the process dynamics are often too complex to capture in quantitative models. In industrial practice, both feedforward and feedback control are used; part of the feedforward control in metallurgical control is based on the tacit, mental models of the operators. Similarly, dealing with complex systems implicit in the industrial ecology approach will require both mechanisms as well. The concept of feedforward control clearly illustrates the need for communication and the provision of comprehensive information to all stakeholders on industrial activities. One needs to understand the interactions in the technological system and take timely action: for example in order to establish whether changes in technological configuration may have undesired by-products; or whether changes in environmental requirements or material throughput result in problems for the current configuration. This particularly holds true for metals, because of the strong interdependence and overlap in metal production routes. As a consequence, the effects of changes to the system can not intuitively be predicated. Therefore quantitative models are needed to provide knowledge to decision-makers: To minimize emissions and maintain metal utility, environmental policy and legislation must shift from today's mainly reactive approaches to more pro-active approaches.

6.4 Can industrial ecology models provide the necessary knowledge?

The adjective "deliberate" in the industrial ecology goal of an industrial development towards sustainability implies at least in part feedforward control . Therefore, it is not surprising that most of the industrial ecology studies involve quantitative descriptions of industrial activities in terms of flows, transformations and accumulations. These descriptions should provide for a "unifying core" of industrial ecology connecting the different prescriptive efforts at different systems levels: From process/product level to the metabolism at national or global level. Through such a co-ordinated effort a deliberate advance towards sustainability can be made. To date industrial ecology tools are available for distinct time and spatial scales. Due to the dynamically linked metal cycles, the system is no longer intuitively understandable - e.g. small changes can have large effects - and tools emphasizing distinct parts of the system can not easily be combined to predict system-wide changes. The production of metals is so interdependent that they can hardly be considered separately, and their control spans various organizational levels. Therefore, a further convergence in the current trends in research and modelling of environment related flows in the physical economy is essential. Such convergence could yield significant benefits with respect to the underlying data collection, access and conformity, and the analytical conformity. In addition, it could considerably reduce the effort of modelling such complex systems. For this reason, the data underlying the quantitative description is reported in detail in the appendices. The data can serve as a solid basis for other studies on metals processing and recovery. In addition, if a model methodology is well defined, data can be collected and published in a structured way. Therefore, an industrial ecology SFA model of the interdependent industrial metal resource cycles is developed that can provide a unifying core to industrial ecology models, as it connects the different system levels. It has been demonstrated that by founding the model on reconciled mass balances of the underlying networks of processes, the model is capable to be able to largely capture the dynamic interdependence of metal production and recycling in models. In this way the flows between the different circuits, but also from and into the environment could be sufficiently estimated to identify possible problems and support decision-making. For the further development of such models it is essential that the metallurgical industry (and the manufacturing and waste industries as well) collects and presents data on the different stages in the metal cycles. Availability of recent data is important considering that the metal ecology is an evolving system.

6.5 Conclusions

Present models and studies in industrial ecology are not sufficient to realize its potentially valuable concepts and ideas. In this section, this conclusion is analyzed using the findings of this Part II. Each of the headings below summarizes an important argument in this explanation.

6.5.1 Sustainability, an emerging system property

Sustainability, the continued welfare of human and other life on earth, is an emerging system property. The designation refers to the fact that sustainability is a property of the system as a whole and that one can not know that the system is sustainable until in fact sustainability has been reached. Sustainability is not a specific system configuration that can be achieved, but rather a property that emerges from the continuous co-evolution of human and natural systems. <Chapter 2>

6.5.2 Connecting the industrial and ecological thinking in industrial ecology

Implementation of industrial ecology in its present form can not lead to sustainability , or realization of its objective. Many in the field of industrial ecology share the view that industrial progress is the central means for environmental progress and advance towards sustainability, but industrial ecology so far has not or only partly bridged the gap between its holistic concepts and the different industrial practices. This obscures technological problems and opportunities and thus their consideration by decision-makers at other levels. Because many of the relationships between industrial activities are determined at process level, the current lack of a solid technological footing in the industrial ecology models, studies and literature inhibits the successful implementation of its strategies and concepts. <Chapter 2>

Industrial ecology is an ecological or systems approach that focuses on a part of sustainability. Based on sustainable examples in nature, ecosystems, it strives to achieve a deliberate (r)evolution of industrial activities within the boundaries set forth by natural systems they are founded on. This deliberate development of industrial systems towards sustainability requires (i) the co-ordination of industrial activities mutually, and with the other activities in the resource cycles, and therefore (ii) the support of decision-making across various organizational levels that influence industrial activities. Two elements can be distinguished in industrial ecology approach: descriptive and prescriptive elements. The descriptive element describes the industrial system at and across system levels. The prescriptive element aims to stimulate decision-making based on considerations of sustainability. To co-ordinate decision-making across system levels descriptive approaches should be able to show a consistent picture of the industrial system at the various levels.

6.5.3 The dynamic interdependence of the metal metabolism

Present MFA studies on metals are insufficient as tools to invoke improvement in their industrial systems. Neither in the industrial ecology literature, nor in metallurgical literature have (SFA) models been reported that showed the dynamics and interconnectivity of the metal resource cycles at the proper resolution. Because the metal production and recycling capacity is realized by a dynamic network of reactors, tools to invoke improvement in this capacity also require modelling at level of reactors. <Chapter 3>

The metal production/recycling system can be considered as an example of industrial ecology in practice. Consequently, the production, use and recycling of different metals (the metal metabolism) is so interconnected that they can not be considered independently and the effectiveness, feasibility and environmental impacts of the different industrial ecology strategies are not intuitively predictable. This capacity is realized by a dynamic network of reactors. modelling at this level of detail requires the use of statistical methods to increase reliability. In particular, data reconciliation methods from engineering practices are essential tools to model at this resolution; to obtain reliable closed mass balances around each reactor type from data sources in literature. The metal wheel is developed to visualize the interdependence in metal production and recycling in a simple manner. It represents the combined capacity of the metallurgical industry to soundly produce high-grade metals from different raw materials and assists in the appreciation of the effect of metal groupings. As such, it can be a valuable tool for industrial ecology models, studies or product designs.

6.5.4 Feedforward control in the metal ecology

Predictive, quantitative models of the system are required to promote feedforward control of the system. These models must be rooted in a solid understanding of technological infrastructure (i.e. representing the system as a dynamic network of reactors) to be able to predict the effect of changes, and introduce the tacit industrial knowledge and the detailed engineering models into the various levels of decision-making. <Chapter 4>

For co-ordination of the production, use and recycling of different metals, two types of control can be distinguished: the reactive feedback and the predictive feedforward control. Feedback control is necessary, because the system of metal production and recycling processes is too complex to fully predict the environmental consequences of technological changes or of new policy and legislation. Feedforward control is to be preferred, because it enables control without offsets in the control objectives. It requires a model that links transformations and flows of materials and energy to the dynamics of the metal metabolism. The effects of changes to the metal metabolism can not be completely modelled using mass balances only, among others due to the complex interdependence between feed composition and product quality in metallurgical processes - partly controlled by tacit knowledge. Striving towards such a model not only provides valuable insights about how the processes interact and how this might affect the environment, but also provides for a basis to include the industrial tacit knowledge (and the detailed engineering models) into the decision-making process.

6.5.5 A predictive dynamic model to control the metal metabolism

Since present MFA studies are not sufficient to invoke improvement, a new type of SFA model was developed. Because this new multi-level dynamic model is rooted in the metallurgical network of reactors, it can estimate the effect of changes in the metallurgy of one metal on the metallurgy of other metals. Through identification of the potential metallurgical constraints in advance, it enables feedforward decision-making at higher system levels. The model developed can invoke improvement by visualizing the constraints of cyclic use of metals and facilitate the inclusion of metallurgical process technology know-how into industrial ecology strategies and concepts. <Chapter 5>

The case on lead production demonstrated that dynamic bottom-up modelling of the interconnected metal production and recycling systems can quantify the dynamic interdependence sufficiently to assist the pro-active evaluation of strategies. The model developed bridges the gap between the detailed process engineering and the holistic industrial ecology models, and provides a basis for feedforward control of metal production system across its system levels. Due to the dynamic interdependence of metal production and recycling, a non-linear, dynamics system results. Consequently, the benefits and constraints of either containment or prevention approaches are not intuitively predictable, neither can they be adequately estimated with linear LCA (or MFA) methods. The model provides a scientific backing to evaluate impact of changes in the resource cycles on the metallurgical system. The model showed quantitatively how bismuth production is linked to the production of lead and copper, and that its production can not independently be changed. The simulations for tin-zinc-bismuth solder showed bismuth production can increase to 453% without changes in the raw materials consumption pattern or without having to find new bismuth sources. This corresponds to an average Bi percentage of 15% in the substituting solder alloys. The models showed that lead substitution is a dynamic problem: the maximum change is dependent on the actual configuration of stock and flows between the different processes. If 10% more lead is recycled this can reduce average bismuth percentage to 14%. The maximum percentage becomes even lower (viz. 7%) for the SnAgSbBi solder, when considering that anode slimes are also consumed by the silver production processes. Feedforward control will become even more important if a further phase-out of lead is considered. In line with the waste prevention principle, lead substitution has become an increasingly popular approach to reduce lead emissions into the environment at the source in Europe. In case of an extended ban on lead, both the availability and recovery of a range of metals will be affected. The phase out of lead can affect not only the containment of lead in the resource cycles, but also the containment of a number of other metals.

6.6 Metal Ecology

To bring industrial ecology concepts out of the philosophy books and into reality, industrial ecologists must expand on this more detailed methodology. Industrial ecologist need to take particular care to ensure sufficient depth in their models. The complex interdependence of industrial systems can not be captured with present "superficial" MFA methods. The model developed represents a first attempt to connect the underlying details of metallurgical processes to industrial ecology strategies such as closing the materials cycles or detoxification. Since the model has a sufficient technological depth to model for feedforward control, recommendations for improvements must lie in the scope of the model. Economic models should be added to the technological model since the price for instance determines the (economic) selection of secondary resources, or the recycling of residues. The model will be further expanded to include interconnection with other (groups of) metals, as their production system shows similar characteristics to that of the metals selected in Part II. Moreover, the approach taken is not unique for the metallurgical industries. The chemical industries for instance, can also be considered a complex network of interrelated processes, which have to cope with comparable problems. Individual processes typically rely on other manufacturing processes for raw materials, and as markets for their products. As a consequence, there are a variety of production routes available for different chemical products. To support decision-making without neglecting the technological constraints and opportunities, the development of these predictive models can be used for series of interdependent chemical processes. The value of these detailed quantitative models can be expected to increase with the implementation of industrial ecology. This will direct the development of society to arrive at a type III ecosystem - the goal of industrial ecology. As a result it will require coping with increasingly interconnected industrial systems, such as the metal production and recycling system, and development of quantitative models as unifying cores for multi-level decision-making involved. Because this is a very data-intensive process, industrial ecologists should clearly define their data requirements and methodologies. Only if a methodology is well defined, data can be collected and published in a structured way. Take thermodynamics as an example: all thermodynamic data are reported in the same manner to ensure consistency within the framework of thermodynamic theory. For representative modelling of metallurgical systems, industry must ensure that the data and flowsheets represent industrial practice and that these are published in literature available to industrial ecologists rather than in specialist or specialist literature alone. The model also can be used to complement other industrial ecology approaches that typically do not go into much detail, such as LCA. To facilitate the use of the results obtained with the proposed model, an alignment of the various impact assessment methods should be facilitated to ensure conformity of the results of the proposed model with requirements of the less detailed approaches. Once again rigour in the theory will make this possible!

Part III

Product Recycling as applied to the Car

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Chapter 7

The dynamic and distributed nature of the recycling rate of the car - a fundamental description of recycling systems

The European Union directive on the recycling of passenger vehicles [9] on the End-of-Life Vehicles (ELV's), imposes strict recovery and recycling targets to be achieved in the nearby future. Calculations to predict the recyclability of the car are required for the type-approval of cars [31], which have to obey to the targets as laid down in the EU directive on passenger vehicles [9]. In view of these legislative constraints, it is essential that the recycling rate of the car can be calculated and predicted. This requires a proper and consistent definition of the recycling rate, which also provides insight into the various parameters affecting the realisation of the recycling rate. It is illustrated that the definition of the recycling rate and the realisation of the imposed targets are very much dependent on different parameters such as the changing lifetime of the product and product design. It may seem obvious that the recycling rate is determined by various time-varying factors; however this chapter endeavours to describe and quantify the role of these factors on the recycling rate over time by the use of a dynamic systems model. Using the dynamic model a definition has been derived for the calculation of recycling rate on a statistical basis, taking into consideration the dynamic and distributed nature of the design of the car. It will be illustrated that this type of approach is a prerequisite to determine the recycling rate of future multi-material super-light car designs. In addition different definitions of the recycling rate will be presented and discussed, discussing the present flawed approaches. This will lead to a better understanding of the parameters affecting the recycling system and a more precise understanding of the recycling targets as imposed by EU legislation. Various simulations will show the influence of the distributed and time-dependent parameters such as the life-time, weight and composition of the car on the recycling rate of the car. This will illustrate that these factors should be considered when defining, calculating and predicting the recycling rate of the car. The theory and models developed will indicate that without any statistics and dynamics involved and the lack of a fundamental technological basis the ISO norm for recycling rate calculation is really useless. Furthermore, all the developed theory is anchored in a Population Balance view to reality and hence requires a good understanding of this theory.

7.1 Introduction

The International Organization of Standardization (ISO) has developed a calculation method for the recyclability and recoverability of the car in view of the EU legislation [36], however the definition and calculations have been derived without any statistics involved and are not based on any theoretical knowledge of recycling and the dynamics and statistics involved and are therefore useless as a basis for the calculation of the recycling rate calculation. In Europe targets have been laid down by EU legislation for the recycling rate of end-of-life vehicles to be achieved within the nearby future (Life cycle, see Figure 7.1). These strict recycling targets are one of the driving forces for more awareness on the importance of recycling in the product's life cycle as well as for the optimisation of recycling systems.

The performance of a recycling system, as well as the effect of optimising it, can be measured based on the achieved recycling rate. Moreover the proposed directive on the type-approval of passenger vehicles requires the calculation and prediction of the recyclability in the design phase on a consistent basis. Of paramount importance in this are:

- the definition of the recycling rate;
- the definition of the parameters influencing this rate as well as;
- the parameters affecting the realisation of the recycling targets.

A consistent definition of the recycling rate, which provides the designer with information on the relation between design and the recycling rate over time, can only be derived based on a fundamental understanding of (the dynamics of) the recycling system and its leading parameters. The definition of the recycling rate and the realisation of the imposed targets are very much dependent on the dynamic, and statistically distributed nature of different parameters in the Resource cycle of the car (see Figure 7.1) such as:

- the changing lifetime of the car;
- changing product design;

of which the combination will determine the input of the recycling system over time.

It may seem obvious that the recycling rate is determined by various time-varying factors; nevertheless this chapter will describe and quantify the role of these factors on the recycling rate over time by the use of a simple dynamic systems model. The dynamic model has to describe the resource cycle system as a dynamic system and has to define the basic principles for a consistent definition of the recycling rate within a statistical framework, representative for the industrial reality of car design and recycling. This model will permit the calculation and prediction of the recycling rate as a function of the numerous parameters describing the behaviour of the recycling system, in combination with changing design scenarios etc., all within the statistics of car design and recycling practice. This dynamic model will establish the link between the Resource cycle of the car with its Life cycle (see Figure 7.1) based on a technological and statistical framework. This discussion will also reveal whether the imposed EU recycling targets are realistic and feasible. It will also indicate that the ISO norm for calculation of the recycling rate is strictly speaking useless.

7.2 Recycling Rates

The term recycling rate is frequently used but its meaning is not always clear. One can still find recycling rates expressed in tons of recycled car or material in a given year related to

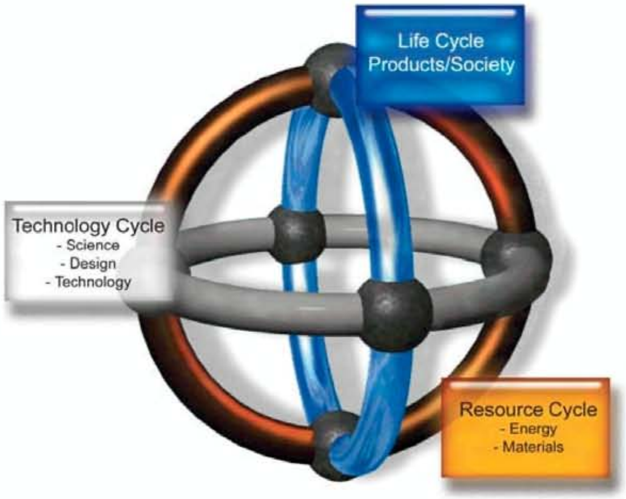

Figure 7.1: Defining the recycling rate of the car - combining the Resource cycle and the Life cycle of the car

(a) the total demand of this material in the same year or (b) the total production in this year. All goods or articles manufactured, however, have their life span. It may stretch from a few days up to several decades. It soon became a common practise to relate, for example, any metallic scrap available for a second usage cycle to the year of its production. However, the year of production for a given category of scrap is in fact unknown, and for collected old scrap there is almost no way to even assess the year of production within an acceptable span of accuracy. Therefore so-called average life cycles are used for recycling rates, although the figures calculated by this method are rather suggestive of reality than accurate.

The "real" recycling rate of a metal should refer the production from secondary raw material (scrap) of the present year to the total production "n" years ago, whereas "n" is a fictitious average lifetime of all goods manufactured from this metal (Eq. 7.1).

$$R_1 = \frac{t_{pp}}{t_{tp_n}} \ (\%) \tag{7.1}$$

where

t_{pp} = present production from secondary material
t_{tp_n} = total production n years ago

Frequently the following definition (Eq. 7.2) of a recycling rate is used i.e. the present production from secondary material divided by the present total consumption.

$$R_2 = \frac{t_{pp}}{t_{ptc}} \ (\%) \tag{7.2}$$

where

t_{pp} = present production from secondary material
t_{ptc} = present total consumption

The most commonly used definition of recycling rate is the present secondary production divided by the present total production (Eq. 7.3).

$$R_3 = \frac{t_{pp}}{t_{ptp}} \ (\%) \qquad (7.3)$$

where

t_{pp} = present production from secondary material
t_{ptp} = present total production

These different recycling rates (Eq. 7.1 to Eq. 7.3) are commonly but rather indiscriminately used in the public and therefore deserve a brief explanation:

- R_1 is a meaningful but purely theoretical figure, for the number of goods and products and their respective differing lifetimes is impossible to determine.
- R_2 is an acceptable figure when used for comparison - although recycling is based on past resources - since the data used are reliably determinable.
- R_3 is a rather meaningless figure, since many European countries Germany satisfy a large portion of their consumption by imports resulting in reduced production (consumption = own production + net imports).

Cadre 7.1
Recycling rate of aluminium

The past aluminium production and consumption of Germany is well documented by the former Metallstatistik of Metallgesellschaft AG. The data published therein are used to evaluate and compare the development of the 3 different recycling rates (Eq. 7.1 to Eq. 7.3) for aluminium in Germany. Table 7.1 depicts a surprising difference between these recycling rates. From R_1 *one can conclude that in Germany presently about 55% of the past aluminium production is re-surfacing as secondary raw material (scrap). Today the share of secondary aluminium production has risen to 49% (*R_3*) while the recycling rate based on consumption (*R_2*) fell from 30 to 20%.*

Table 7.1: Aluminium in Germany, n = 5 - 10 - 15 - 20 years

units (10^3 t/a)	2001	1996	1991	1986	1981
Primary production	652.0	576.5	690.3	763.7	728.9
Secondary production	623.0	416.9	541.6	482.5	397.5
Total production	1275.0	992.4	1231.9	1245.8	1126.4
Total consumption	2820.0	2176.2	1884.7	1653.3	1325.6
R_1 (%)	-	62.80	50.60	50.00	55.30
R_2 (%)	48.90	42.00	44.00	38.70	35.20
R_3 (%)	22.10	19.20	28.70	29.20	30.00

The recycling rate of the aluminium inventory in a given sector/branch is a product of:

- *Collection rate CR*

- *Pre-melting yield PY*
- *Melting yield MY.*

where:

CR *t scrap collected/t scrap inventory; this figure is specific for branches and countries as well*

PY *t scrap delivered to refiner (+ remelter)/t scrap collected and delivered to scrap processors*

MY *t metal produced/t scrap fed to refiners (+ remelters).*

The total recycling rate RR (t metal produced/t scrap inventory) of any inventory is thus given by Eq. 7.4.

$$RR = CR \times PY \times MY \tag{7.4}$$

Irrespective to an eventual definition of a recycling rate one fact should be considered in any case: Part of the European demand for aluminium is used in sectors, in which the aluminium is converted into compounds fundamentally inaccessible to recycling. E.g. aluminium used as chemical compound (like $Al(SO_4)_3 \cdot 18H_2O$*), aluminium metal for alumino-thermal winning of metals (like Mn, Cr, Mo, W), for sacrificial anodes, for deoxidation of steel , for fireworks or as rocket propellant. In all such cases aluminium is converted into a compound which cannot be reduced to metal or is irrecoverably dissipated. Roughly 6% of the European aluminium consumption is used in such sectors. Hence the recycling rate* R_2 *has to be referred to just 94% of the present total consumption, which represents the real base for basically recyclable aluminium. Consequently* $R_2 = 23$ *to 32%. But any figure within this wide range of potential interpretations of a recycling rate does not reflect reality. Table 7.2 depicts the present figures on life span of aluminium good categories used in official statistics. [48]*

Table 7.2: Life span of aluminium good categories

Field of Application	Average Life Time (yrs.)
Automotive	10 years
Machine construction	10 years
Electrical engineering	10 years
Building construction	10 years
Chemical and food industry	5 years
Packaging	2 years
Household goods	4 years
General metallic goods	5 years
Other application	5 years

These figures indicate a substantial amount of statistical data, however, the use of these data for the calculation is still not helpful and not recommended:

- *The average lifetime of aluminium goods in cars in Europe is presently about 14 years. But this figure is statistically misleading. In fact it means that today 50% of all de-registered cars are on average older than 14 years, and 50% are younger, and scrap stemming from car recycling could be 1 month or 35 years old.*
- *The lifetime of aluminium goods for air planes and rail road train cars - all covered by automotive industry - is definitely different from that of cars.*

- *The lifetime of aluminium from buildings is not even in average assessable. The only reliable statement is that 10 years is rather unrealistic. Aluminium profiles in windows and doors e.g. have an average lifetime of 26 years. Other goods may easily last until a building is demolished, i.e. that scrap could be as old as 50 years.*

The term recycling rate is in fact a multiplication of the "collection rate" and the "recovery rate". The collection rate expresses the amount of residual material channelled back into the utilisation cycle related to the total available amount of this residual material. A recovery rate would be the amount of metal extracted from processed or unprocessed scrap related to the metal content of this scrap.

Due to particular consideration of the necessary purity and cleanness of the scrap the demolisher is collecting only 138 t of aluminium goods, and skipped all those articles which were very small and/or heavily contaminated by plastic and/or foreign metals. Now the sample melt produced a yield of 95%, corresponding to about 97% metal content. The recycling rate in this case is 138/150 x 0.97 = 89%. This example demonstrates that recycling rates without its definition are meaningless - or at least subject to misinterpretation.

Data about recycling efficiency of a metal should cover the following aspects:

- *Application in different branches*
- *Collection rate of scrap from these branches*
- *Assessed or assumed lifetime of goods in these branches (years), expressed as average or as distribution curve (e.g. bell shaped curve)*
- *Average growth rate of demand.*

With such data a much more meaningful and in particular transparent calculation of recycling rates can be produced, which can be compared with that of other metals provided they are calculated likewise. Table 7.3 is based on aluminium data which are artificially created, and do not refer to any actual country or year, but explain sufficiently the principles of calculation. The distribution of aluminium use refers to the present year.

Table 7.3: Recycling efficiency data for aluminium (artificial)

Field of Application	Distribution (%)	Collection Rate (%)	Scrap Available (%)	Average Life Time (y)
Automotive ind.	24	72	17.3	15
Machine construction	7	60	4.2	10
Electrical engineering	11	83	9.1	13
Building construction	18	90	16.2	25
Chemical, food ind.	2	80	1.6	4
Packaging	8	25	2.0	2
Household goods	10	75	7.5	4
Other applications	20	65	13.0	8
Total	100		70.9	13.7

In this case the average collection rate is 70.91%. An average recovery rate of such collected scrap is here assumed to be in the order of magnitude of 87%, which means that 70.91 × 0.87 = 61.7% of the aluminium delivered to these branches can be returned again as metal into the *next utilisation cycle. If one assumes further, that aluminium demand increased during the last 30 years by an average of 2.75%/year, then a "standard" recycling rate can be calculated. 70.91 x 0.87 /(100/(1+0.0275)13.67 = 89% of the metal originally consumed by the various branches is returned as metal to a new utilisation cycle. This recycling rate is based on the incorrect assumption, that during the past years the fractional distribution of aluminium consumption by the different branches has been constant. Nonetheless, this recycling rate is transparent; the basis is well defined and is therefore applicable to meaningful comparisons between metals. In a more broader sense the collection rate defines how much of a material from a branch - it could be more narrowly defined as aluminium in beverage cans only or more globally as total copper in electrical industry - is offered for recycling processes, the recovery rate defines the losses in the subsequent recycling processes.*

7.3 Directive 2000/53/EC on ELV's

The Parliament of the European Union has approved a directive for the product responsibility on passenger vehicles. In this directive, targets on the recycling of passenger vehicles have been laid down [9]. In article 7.2 it is stated for all end-of-life vehicles: "*that no later than 1 January 2006 the reuse and recovery shall be increased to a minimum of 85% by an average weight per vehicle and year. Within the same time limit the reuse and recycling shall be increased to a minimum of 80% by an average weight per vehicle and year. For vehicles produced before 1 January 1980, Member States may lay down lower targets, but not lower than 75% for reuse and recovery and not lower than 70% for reuse and recycling. Moreover, no later than 1 January 2015, for all end-of-life vehicles, the reuse and recovery shall be increased to a minimum of 95% by an average weight per vehicle and year. Within the same time limit the reuse and recycling shall be increased to a minimum of 85% by an average weight per vehicle and year*". A summary of the imposed targets on the recycling and the type-approval for new vehicles (Article 7.4) can be found in Table 7.4 and Table 7.5. [9]

Table 7.4: Targets EU directive for the recycling of End-of-life vehicles

Year	Recycling targets	
2006	Reuse and recovery	85% by an average weight per vehicle and year
	Reuse and recycling	80% by an average weight per vehicle and year
2015	Reuse and recovery	95% by an average weight per vehicle and year
	Reuse and recycling	85% by an average weight per vehicle and year

Table 7.5: Targets for the type-approval of new vehicles

Year	Targets for the type-approval of new vehicles	
01.01.2005	Reuse and recovery	95% by weight per vehicle
	Reuse and recycling	85% by weight per vehicle

It must be noted that the EU directive as given above uses "weight" in the definition of the targets, which is strictly speaking the 'mass' of the vehicle. For reasons of consistency this work will therefore speak about the "weight" (in kg) of the vehicle, when in the fact the 'mass' of the vehicle is described. Moreover this work will consistently speak about 'recycling rate' and 'recycling targets' when referring to the targets for reuse, recycling and recovery as imposed by the EU legislation. The "recycling rate" therefore refers to the sum of reuse and recovery (including recycling) of materials/energy from passenger vehicles.

7.3.1 EU definition of the recycling rate of the car

For the assessment of recycling systems as well as the understanding and realisation of the EU recycling targets, an accurate definition of the recycling rate and its parameters is a prerequisite. When properly defining the recycling rate a consistent basis is created, which provides insight into the fundamental characteristics and performance of recycling systems. A commonly accepted definition (also used as the basis for EU legislation) states that the recycling rate is equivalent to the ratio between the weight of the recycled material from a given application at a certain moment in time and the total weight of the same application available for recycling at that moment in time. However, this definition is still very general and does not give detailed insight into the definition of the recycling rate and its role in representing the performance of recycling systems and the parameters affecting this.

The imposed EU recycling targets on end-of-life vehicles are defined based on the average weight per vehicle per (dismantling) year (see Table 7.4). The weight and composition of the car at the time of production initially determine this weight. However the time span between production and dismantling determines the weight of the input of the recycling system at the time of dismantling. This delay between production and dismantling is determined by the lifetime of the product. In order to define the recycling rate of the car, it is essential to understand the various parameters playing a role in the production, design, life time and use of the product and their influence on the weight and composition of the car at dismantling.

The definition of the actual weight of the recycled/recovered material is still very much subject to political discussion and for this reason not clearly defined by legislation yet. In the EU directive on end-of-life vehicles the recycled weight is subdivided into three different categories: reuse, recovery and recycling. However in practice it is not always apparent to which of these categories a certain unit operation in the recycling of end-of-life vehicles contributes. An example is the ongoing discussion on the contribution of incineration to recycling. Incineration can be defined as a recovery operation, however it is often regarded as disposal and does therefore not contribute to the recycling targets. Verhoef et al. [197] discussed this for the incineration of waste, a discussion that also applies to end-of-vehicles. This definition could have a major impact on the feasibility of the imposed recycling targets especially in view of the changing composition of the car, which will consist of more plastics, for which incineration with energy recovery could be a viable processing route.

An additional complicating issue is that there are various ways to determine the actual weight of recycled or recovered material. In the EU document on the management of end-of-life vehicles it is stated that 75% of end-of-life vehicles, being the metal content of the car, is recycled. The same statement is made by the International Organization of Standardization [36] when defining a calculation method for the recyclability and recoverability of passenger vehicles. This implies that the metal content of the car is recovered for 100%. This statement indicates a lack of knowledge on the performance of recycling processes, since due to the interrelation between grade and recovery of mechanical separation processes (which implies that both high recovery and grade requirements cannot be fulfilled at the same time) [32] the recovery of materials will always be lower than 100%, if the quality of recycled materials has to be increased by mechanical separation. A high quality feed to metal producing processes is of critical importance to ensure the economic production of high quality metal products after (s)melting, which is indispensable in achieving high recycling rates [33]. The recovery of metal producing processes is constrained by the prevalent thermodynamics and kinetics [33].

Therefore, in metallurgy, the recovery of the metal will also always be lower than 100%. High environmental standards and recovery rates can only be achieved and maintained through proper understanding of the complex interactions in recycling systems, which are strongly dominated by continuously changing product design. This discussion immediately reveals the various parameters such as design, efficiency of physical separation and metallurgy playing an important role in achieving high recycling rates, and therefore in setting up a detailed definition of the recycling rate of products based on proper knowledge of recycling theory and practice.

7.3.2 Literature definitions of the recycling rate

Some work has been done on the definition of recycling and recyclability of products with respect to the EU legislation. For example Villalba et al. [288] defines recyclability as the ability of a material to reacquire the properties it had in its virgin state. It is stated that the recyclability can be estimated by its devaluation, based on the loss of monetary value. This quantification of recyclability does however not express the actual amount of recycled materials, which can find its way back into the material cycle. This method has therefore no value for EU recycling policy, in which the defined recycling targets are weight based. Moreover, from this definition, it does not become clear which parameters are of influence on the recyclability (based on weight) of a product. Sander et al. [289] discuss how the weight of the different variables in the EU recycling/recovery rate should be determined, e.g. what is included in the weight of the car (fuel, accessories, etc.) and how should this be measured in practice, how should the amount recycled material be determined, what are the system boundaries of EU legislation, etc. Although it is necessary to come to a uniform basis on this in defining the recycling/recovery rate of cars, no definition is given by Sander et al. [289], which includes the discussed parameters into the calculation of the actual recycling rate over time. Kalisvaart et al. [290] discusses the choices and alternatives in defining the recyclability of products.

Liu et al. (2002) [291] discusses a recyclability assessment model based on an artificial neural network in which the recyclability of a product is related to its design based on consultancy of experts and specialists. The approach presented is not based on a fundamental technological description and understanding of recycling systems, the role of the quality of recycling intermediate products, etc. and is subjective; summarised recycling is presented in a far too simplified manner, which makes the assessment of recyclability and design for recycling debatable. No recyclability values were produced from the simulations presented. It is important to notice that the neural network can only predict the output (= recyclability) within the boundaries of the trained (expert) data set. No extrapolation for future scenarios or car design could be applied, while at the same time guaranteeing the credibility of the output.

The International Organization of Standardization [36] defines a calculation method for the recyclability/reusability and recoverability/reusability rate of road vehicles to be used as an international standard for assessing the ability of new vehicles to be recovered/recycled. In this report, however, the recyclability and recoverability rate are simply defined as the ratio between the sum of the mass of materials reused/recycled/recovered during dismantling, metal separation and non metallic residue treatment and the 'complete vehicle kerb mass' at end-of-life defined in ISO 1176 [292] . The calculation method presented by the International Organization of Standardization is a single value, static approach, which is not based on detailed knowledge of end-of-life separation technology and metallurgical processing as the basis for the defined variables in the recyclability/recoverability rates (e.g. the metal content

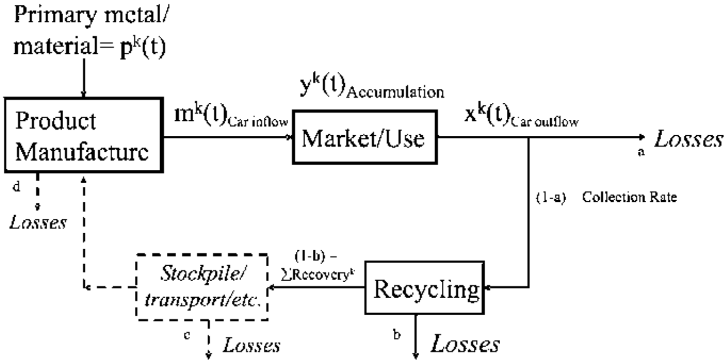

Figure 7.2: The architecture of the dynamic model to define the recycling rate for cars (a, b and c are mass fractions between 0 and 1) [2]

is considered as being fully recyclable, which is not the case due to prevalent physics, thermodynamics and kinetics). The presently defined methods are not based on any theoretical knowledge on the complex behaviour of recycling processes and present therefore a far too simplified picture for the assessment and calculation of recycling rates. The complex interaction between the design of the car and the final material recovery over time is not addressed in this method for assessing the ability for recycling/recovery (new) vehicles. In all of the studies mentioned a first principles description of recycling systems within a statistical framework as well as the performance of recycling processes is lacking. This is the only basis on which the recycling/recovery rate of a product can be properly defined and calculated.

7.4 Dynamic modelling of the resource cycle of end-of-life vehicles

The resource cycle of products consists out of many different stages, such as production, use and recycling, which are closely related and each play a crucial role in the behaviour of the total system over time and therefore inherently affect the (definition of the) recycling rate. The resource cycle and its parameters playing a role in the different stages of the cycle (e.g. design, life time, recycling rate) are not fixed, but will change continuously over time. In order to come to a fundamental description of the behaviour of recycling systems within the interconnected resource cycle system a dynamic model has been developed, representing the various stages in the resource cycle of a product and its dynamics and their role in the definition and achievement of the recycling rate (see Figure 7.2).

The dynamically changing link between end-of-life products, their design and use is defined based on the dynamic model, which describes the resource cycle of cars [2]. This model permits the visualisation of the influence of various time-varying and at the same time statistically distributed parameters on the recycling rate over time. In addition this model also permits the formulation of an improved definition of the recycling rate on the basis of a fundamental description of the resource cycle and the imbedded recycling system. The description and optimisation of the resource cycle and in other words the recycling of modern consumer products is only possible with a detailed understanding of the total material recycling system as a dynamic feedback system. Dynamic modelling has been part of environmental engineering for a long time, as illustrated by many publications in this field. De Haes and Van der Voet [41] distinguish three types of models for the modelling of flows and stocks, amongst which dynamic modelling. McLaren et al. [293] discuss for example the use of a dynamic modelling approach to determine the environmental impact of recycling based on energy analysis. However, only a changing recycling rate and corresponding scrap collection energy were taken into consideration in a relatively simple dynamic model, which does not include a comprehensive insight into the assessed recycling system. Moll [294] uses dynamic life cycle modelling as a tool to evaluate sustainable development. This study on dynamic modelling, like various other authors, only uses single value data (averages) as the basis for the model. However, the recycling data is inherently distributed, which no author considers. Moreover the time-varying influence of the distributed nature of data e.g. changing product design (weight and composition), changing recycling rates in combination with time delays in the system (due to life time of products or stockpiling of the materials) have not been included in assessing the recyclability of products in any study when e.g. determining the environmental impact of recycling, excluding the complexity of technology. The recycling system has not been described in detail on process level in these environmental studies. Therefore, the complex dynamically changing interrelationship of product design and the recyclability of a product have not been addressed in the numerous studies on environmental modelling. In order to describe the role of the various stages in the resource cycle of passenger vehicles as depicted by Figure 7.2 on the recycling rate of the product only the market/use and recycling phase of the model will be investigated in detail. This approach permits a detailed investigation into the characteristics of the various parameters building up the resource cycle and their effect on the (definition of the) recycling rate.

7.4.1 Statistical nature of the resource cycle of products

Distribution of the lifetime of cars

The purely statistical nature of the average lifetime of cars and the modelling of their recycling is illustrated by data for de-registered cars in The Netherlands as published numbers of ARN [295]. Figures 4.3 and 7.3 represent these data, which reflect the number of end-of-life vehicles originating from different years of production, being the source for car scrap recycling in the years 1997-1999. The statistical nature of the life time of products was also discussed by Melo [296], who developed a statistical analysis to determine the aluminium metal scrap generation. The number of end-of-life vehicles in The Netherlands as a function of the year of production and for the years of dismantling 1997 to 1999 is depicted by Figure 4.3 [295].

Figures 4.3 and 7.3 show that the data can be described mathematically by using a Weibull distribution function defined by two parameters alpha (α) and beta (β) (Eq. 7.6). Besides a Weibull distribution, other functions such as a Normal and Gamma were considered to describe the data of Figures 4.3 and 7.3. Due to the fact that the Normal distribution has a basic symmetric shape and ranges between minus and plus infinity, it cannot be applied to describe these data in a proper way, however, the Gamma and Weibull functions can describe a wide variety of distribution data. The Weibull distribution has been selected to describe the data as represented in Figures 4.3 and 7.3 as this provided the best fit for these data, which was in excess of R^2=0.98.

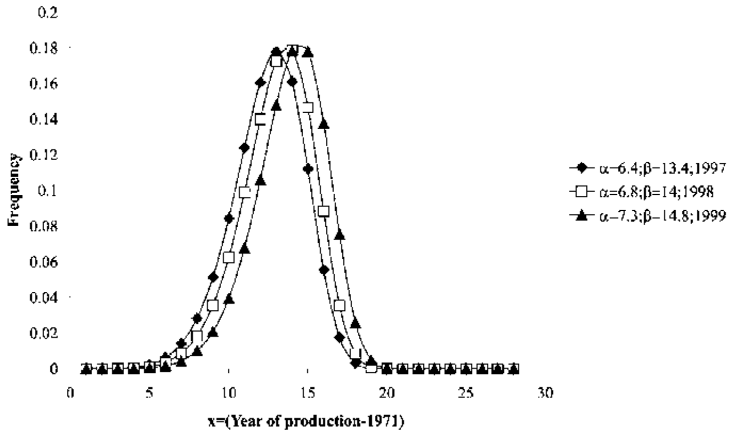

Figure 7.3: Weibull distribution function for the fraction of cars returning at a particular (dismantling) year 1997-1999 as a function of the production year (t=year of production-1971) fitted for the normalised data of Figure 4.3

$$f(t,\alpha,\beta) = \frac{\alpha}{\beta^{\alpha}} \cdot t^{\alpha-1} \cdot e^{-\left(\frac{t}{\beta}\right)^{\alpha}} \tag{7.5}$$

where

t = (year of production - 1971)

Melo [296] discusses the lifetime modelling of aluminium containing products. Instead of using a complete dataset on the lifetime of a product, as discussed here, Melo [296] approached the intervals of the lifetime of aluminium applications, by taking the minimum and maximum average age of the product at disposal, due to the absence of historical data on the age of products upon disposal. Melo discusses the modelling of the lifetime to estimate the potential arising of scrap by using a normal, a Weibull and a beta distribution. The results obtained show that the proposed models yield better estimates than commonly used approaches that assume a fixed life time for products. The changing life time distribution over time was not addressed in this study. It becomes clear from Figures 4.3 and 7.3 that the data on discarded vehicles can be presented by distribution curves as a function of the year of production. If such curves represent the actual situation for (a) given dismantling year(s), it can be concluded that the number of cars produced in a certain year will return as de-registered/discarded old cars, following similarly shaped curves as a function of the year of dismantling. Furthermore, for each year of production a similar curve can be drawn as a function of the year of dismantling. As a result it would be clear that the 3-dimensional Figure 7.4 can be created, which depicts the series of distribution curves each representing the number of cars to be dismantled of each production year for the different years of dismantling. The two time axes represent the years of dismantling (=de-registration) and the years of production (=manufacturing).

An ideal model, which assumes that the data are smooth and lack any disturbances, untypical characteristics for market behaviour, is used deliberately to place the discussion here on a statistical basis. From Figures 4.3 and 7.3 it can be concluded that the fundamental

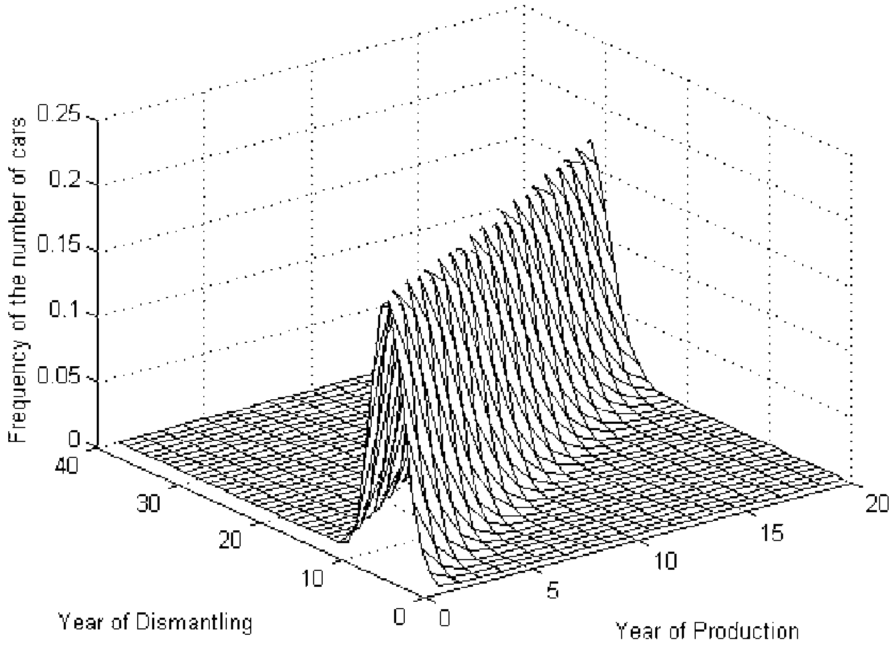

Figure 7.4: Weibull distribution function $f(t_1, t_2)$ of the Year of dismantling $(YD)t_2$ and the Year of production $(YP)t_1$. The average lifetime of a car for these Weibull distribution functions varies from 7.6 years in year $t_1 = 1$ (=1981) to 13.1 years in year $t_1 = 20$ (=2001) determined by a changing α and β of the Weibull distribution (based on data in Figures 4.3 and 7.3)

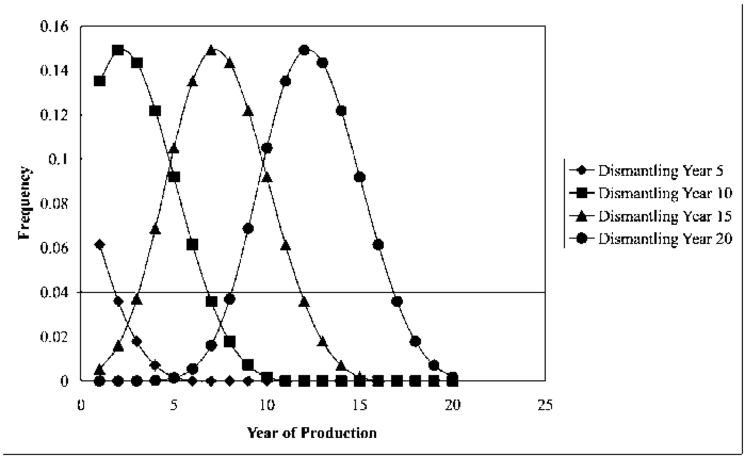

Figure 7.5: Distribution of cars as a function of Year of production derived from Figure 7.4 for the respective Year of dismantling (Absolute Year of production add the year 1981)

shape of the distribution curve for cars, is very realistic, since it is based on national statistical data. Since the lifetime of cars is increasing over time as becomes clear from the normalised data of Figure 4.3, the shape of the distribution curves for the different years of production is changing, defined by changing values for α and β in Eq. 7.6 (depicted by Figure 7.3). In order not to complicate the discussion too much here, the assumption has been made that the same lifetime distribution is valid for all different types of cars, which is not necessarily the case. Figures 4.3 and 7.3 can be explained as being the cross-section through the series of Weibull distribution curves for a particular dismantling year. Those year-by-year cross-sections allow calculating the number of cars of each production year summing up to the "scrap portfolio" of this particular dismantling year. The amount of cars originating from a range of production years, coming available for recycling in a specific year of dismantling can be determined from Figure 7.4. Figure 7.5 is derived from Figure 7.4, depicting the distribution for a dismantling year as a function of production years, which are once again Weibull functions.

Distribution of the weight of cars

The weight and composition of cars have changed significantly over the last 50 years, due to changing regulation on safety, consumer demands on comfort, and the reduction of fuel consumption, to name a few. The statistical nature of the weight of the car is illustrated by data on the amount of cars in different weight classes originating from a certain year of production driving around in the Netherlands on 1-1-2002 [297]. In other words, the data reveals the weight distribution of cars for the various production years presented. Figures 7.6 and 7.7 show that normalised data on the weight of the car for the different years of production can be represented by a Weibull distribution, revealing the increasing weight of the car over time.

The distribution of the changing weight of cars for the different production years can be presented by a 3D-Weibull distribution function $g(t_1, w)$ as depicted by Figure 7.8, where a changing α and β describe the changing distribution over time. The two axes represent the

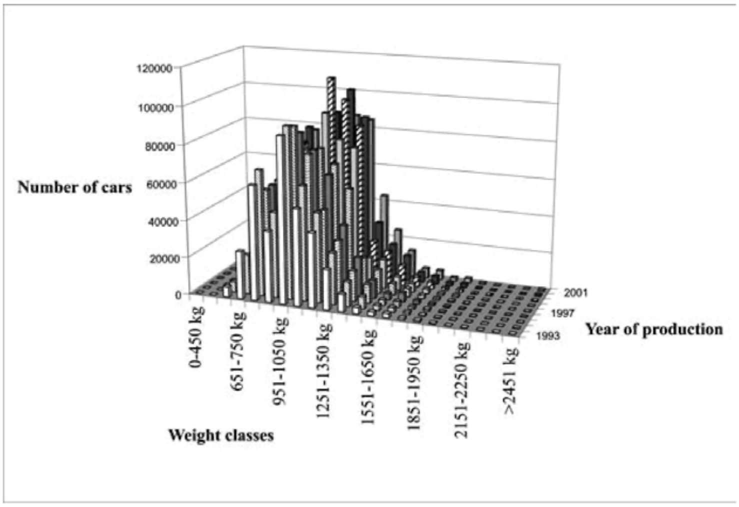

Figure 7.6: The number of end-of-life vehicles in The Netherlands at 1-1-2002 as a function of different weight classes for the years of production 1993 to 2001 [297]

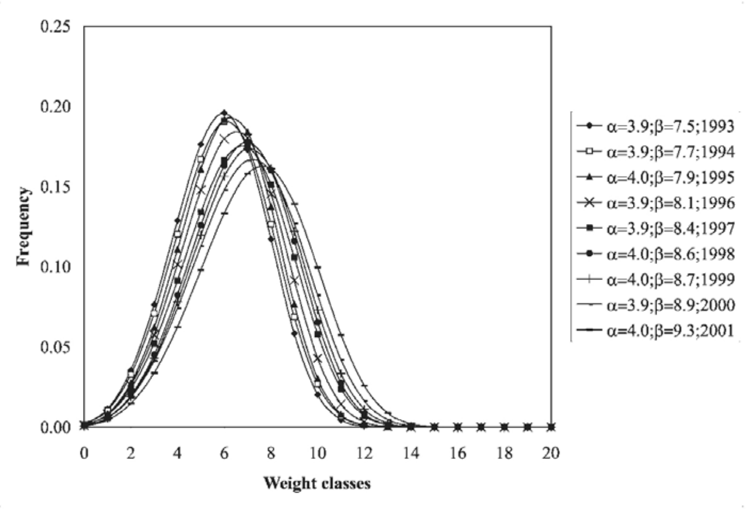

Figure 7.7: Weibull distribution function for the fraction of cars as a function of the different weight classes for the various years of production, fitted for the normalised data of Figure 7.6. (Weight class 0 (0-450kg) - Weight class 20 (2351-2450kg))

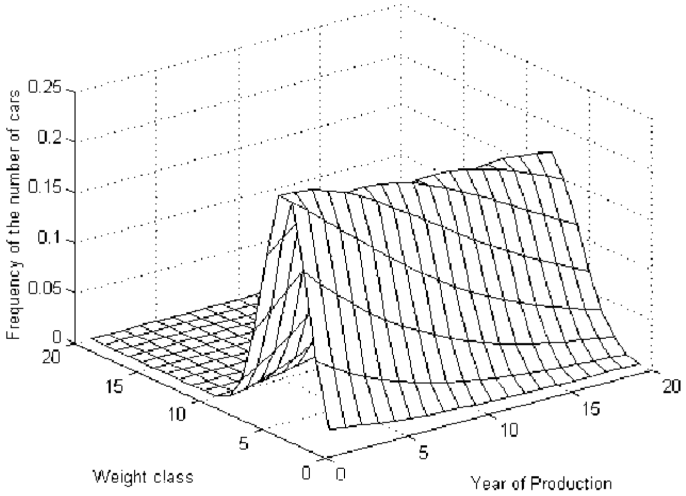

Figure 7.8: Weibull weight distribution $g(t_1, w)$ of cars as a function of Year of production t_1 and weight class w. The average weight of a car for these Weibull distribution functions varies from 856 kg in year $t_1 = 1$ (=1981) to 1207 kg in year $t_1 = 20$ (=2001) determined by changing the parameters of the Weibull distribution (based on data in Figures 7.6 and 7.7)

weight given in weight classes and the years of production. When combining and integrating Figures 7.3, 7.4,7.6 and 7.7, the total weight of the cars available for recycling in different years of dismantling can be calculated.

Distribution of the material composition of cars

Due to improved design to comply with e.g. stricter safety regulation, reduction of emissions during use and changing consumer demands on comfort, the composition of cars is continually changing. Table 7.6 summarises the changing average composition of the car over time for some key materials/elements.

Table 7.6: Change in the average composition of the car [38]

Year of production Component	1965 [%]	1985 [%]	1995 [%]
Steel	76	68	63.5
Aluminium	2	4.5	7
Other non-ferrous metals	4	3	3
Polymers	2	10	12.5
Others	16	14.5	14
Total	100	100	100

The mass percentage of the different elements present in different production models of

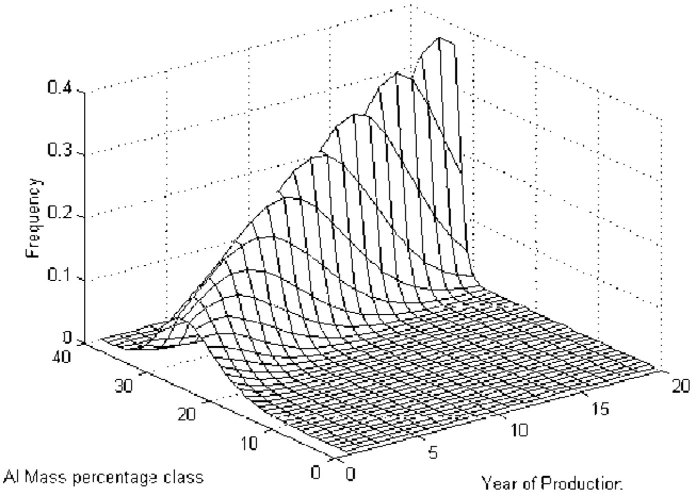

Figure 7.9: Weibull mass percentage distribution $h^k(w, mp^k, t_1)$ (k=aluminium, w=10) in the car as a function of Year of production t_1 and Al mass percentage class mp represented for one specific weight class $w = 10$. The average Al mass percentage of a car for these Weibull distribution functions varies from 6.42% in year $t_1 = 1$ (=1981) to 8.26% in year $t_1 = 20$ (=2001) for w=10 determined by a changing α and β of the Weibull distribution (for mass percentage class 1 (mp=1) the aluminium content is 0.25%, for mass percentage class 40 (mp 40) the aluminium content is 10%)

cars is not only changing over time but is obviously distributed as a function of car model. This distribution is theoretically depicted by Figure 7.9, based on the trends in the data of Table 7.6. Since the composition of the car differs for the different weight classes i.e. different production models of cars, a Weibull distribution function of the composition of the car $h^k(w, mp^k, t_1)$ is defined for all elements k (k=steel, aluminium, copper, polymers, etc.) for each of the weight classes w as given in the weight distribution $g(t_1, w)$.

Combination of distribution functions

The complexity and extremely distributed character of the design and recycling data in practice becomes clear when e.g. looking at the German car production and disposal situation. For Germany, the presently biggest European individual car inventory of approx. 42 million cars, various reliable car production and disposal data exist [298]. From these data it could be deduced that the 42 million cars stem from 139 different manufacturers. Even if each of the car manufacturers has produced only 4 models every 5 years the car inventory in Germany (at this moment) stretches over at least 30 years of manufacturing and consists most likely of more than 3300 different models of cars. Furthermore each of these models has a different weight and shows different contents of valuable materials and components, with different recycling rates. For each of these models the above-depicted curves are applicable, with each their specific lifetime figures. This is still a simplified picture of the real world of recycling cars.

Nevertheless, it gives an indication of the enormous complexity associated with modelling the recycling of cars and the effect the distributed nature of the data could have on the number of cars in circulation and hence also on the achievable recycling rate.

Distribution functions and definition of the recycling rate

It is fundamental to recycling to realise that Figure 7.3 to Figure 7.9 have a strong influence on the recycling rate of the car and obviously on the behaviour of the recycling system. Failing to realise this will lead to erroneous definitions for the recycling rate to be formulated. The average weight per vehicle and (dismantling) year is the basis for the definition of the recycling rate as imposed by the EU directive (Table 7.4 and Table 7.5) and represents the material tonnage used in the car at the time of production coming back for recycling in different dismantling years. As is clear from the previous discussion, the average weight and composition per car per year of dismantling is determined by the distribution functions as defined above, representing the amount of cars originating from a range of production years (Figure 7.3). For each production year a specific weight distribution and corresponding composition distribution are defined in Figure 7.8 and Figure 7.9. By combining the three different distributions for the life time, the weight per production year and the composition per weight class and production year, the (average) weight of the car at dismantling can be determined, which forms the basis for EU recycling legislation. The changing weight and composition is directly related to the maximum achievable recycling rate. A minor change in the percentage and combination of metals present in the (end-of-life) passenger vehicle can have a significant consequence on the final recycling rate, due to e.g. physical, thermodynamic and kinetic restrictions of the separation and metallurgical processes, which are essential in closing the material cycle. It is therefore of utmost importance to be able to translate the consequences of rapidly changing design (described by the distribution functions of Figure 7.3 to Figure 7.9) into the definition of the recycling rate of the car or any other product. The dynamics of any recycling system are defined and described by the discussed distributions. The role of the various distributions in the definition of the recycling rate will be explored in the next section with the aid of a dynamic model, using the defined distribution functions. This model describes the changing weight and composition of the car at production and dismantling over time as a function of the various distributions, integrated into the definition of the recycling rate. The model and the derived definitions provide a tool, which not only makes it possible to determine the trend of the changing recycling rate but also to quantify the actual recycling rate over time as a function of changing car design. A proper definition of the recycling rate based on a fundamental description of the resource cycle provides the basis for assessing the performance of recycling systems. The role of the time-varying parameters as well as the role of statistics in the realisation of the recycling targets will therefore become transparent through this approach.

7.5 Formulation of model and definition of recycling rate

The dynamic model as depicted by Figure 7.2 will be used here to describe the continuously changing weight and composition of the car as a function of the life time of the car as defined in Figure 7.3 to Figure 7.9, and therefore their role in the definition of the recycling rate and the realisation of the EU recycling targets.

7.5.1 Dynamic model

The dynamic model describes and predicts the behaviour of the resource cycle system and the material flows within this system over time as depicted by Figure 7.2. The total weight of the materials produced in the car $m^k(t)$ (Figure 7.2) is determined by the amount of produced cars per year; and the weight distribution and the average mass percentage for the different elements k in the car for each of the different weight classes as derived from the mass percentage distributions. Moreover the weight of the materials flowing out of the use phase $x^k(t)$ (Figure 7.2) is a function of the lifetime distribution of the cars. Eq. 7.6 determines the weight of the different elements $y^k(t)$ in the car accumulating over time in the market/use phase (Figure 7.2). The weight and composition of the car at dismantling $x^k(t)$ is described by Eq. 7.6.

$$\frac{dy^k(t)}{dt} = m^k(t) - x^k(t) \tag{7.6}$$

where

$$\begin{aligned} m^k(t) &= \int_{t_1=t}^{t+\Delta t} \int_{w_1}^{w_2} \int_{mp_1^k}^{mp_2^k} C(t_1) \cdot mp^k \cdot h^k(w, mp^k, t_1) \cdot g(t_1, w) \cdot \\ &\qquad dmp^k \cdot dw \cdot dt_1 \qquad (7.7) \\ x^k(t) &= \int_{t_2=t}^{t+\Delta t} \int_{t_1=0}^{YP} \int_{w_1}^{w_2} \int_{mp_1^k}^{mp_2^k} C(t_1) \cdot mp^k \cdot h^k(w, mp^k, t_1) \cdot g(t_1, w) \cdot f(t_1, t_2) \cdot \\ &\qquad dmp^k \cdot dw \cdot dt_1 \cdot dt_2 \qquad (7.8) \end{aligned}$$

where

$$\sum_{k=Al,steel,Cu,plastics,etc.} \int_{mp_1^k}^{mp_2^k} mp^k \cdot h^k(w, mp^k, t_1) \cdot dmp^k = 100 \tag{7.9}$$

The various distribution functions for the life time, weight and composition of the car have been translated into MATLAB®6.1 (see Appendix C.1). By implementing a Runge-Kutta method from MATLAB 6.1 as well as suitable numerical integration technique Eq. 7.6 can be solved [235]. By this the composition of the car and the weight of the different components of the car at production and dismantling can be calculated as well as the amount of cars and corresponding material content locked up in the system.

7.5.2 Definition of the Recycling Rate (RR)

Eq. 7.6 defines the amount of material that is retained in the use phase of the car i.e. the material not available for recycling, as well as the weight and composition of the car at production ($m^k(t)$) and dismantling ($x^k(t)$) as a function of the various distributions. Based on Eq. 7.6, the recycling rate of the car at dismantling (End-of-life) can be defined by Eq. 7.10, which represents the EU definition of the recycling rate. However, by defining the distributions, which determine the average weight and composition of the car at year of dismantling t_2, Eq. 7.10 will give totally different values for the recycling rate compared to the EU definition or as expressed in the ISO standards [36].

$$RR_{EoL}(t) = \frac{A}{B} \cdot 100\% \tag{7.10}$$

$$= \frac{\sum\limits_{k=Al,steel,Cu,plastics,etc.} (C)^k}{\sum\limits_{k=Al,steel,Cu,plastics,etc.} (D)^k} \tag{7.11}$$

$$= \frac{CR \cdot \left(\frac{\sum\limits_{k=Al,steel,Cu,plastics,etc.} x^k(t) \cdot Recovery(x^k(t))^k}{N(t)} \right)}{\left(\frac{\sum\limits_{k=Al,steel,Cu,plastics,etc.} x^k(t)}{N(t)} \right)} \cdot 100\% \tag{7.12}$$

where

$$N(t) = \int\limits_{t_2=t}^{t+\Delta t} \int\limits_{t_1=0}^{YP} C(t_1) \cdot f(t_1, t_2) \cdot dt_1 \cdot dt_2 \tag{7.13}$$

where

A = average weight of recycled/recovered material per vehicle and year
B = average weight per vehicle and year
C = average weight recycled/recovered component k per vehicle and year
D = average weight of component per vehicle and year

As is clear from Eq. 7.10, the recycling rate at end-of-life is determined by the various distributions as defined previously, giving the changing weight and composition of the car at dismantling over time. Eq. 7.6 and Eq. 7.10 show that the recycling rate cannot be represented by an average or single value as required by EU legislation, but is largely dependent on the distributed nature and therefore the standard deviations of the time-varying lifetime, weight and composition of the car. Therefore, the answer produced by the model (Eq. 7.6 and Eq. 7.10) is an average plus an associated standard deviation. In this equation the collection rate CR is determined by humans and collection systems ($(1-a)$ in Figure 7.2), whereas the recovery rate of each element k ($(1-b)$ in Figure 7.2) is defined among others by the (feed to) the physical recycling and metallurgical plants, therefore by $x^k(t)$. The recovery will obviously be different for the various elements in the car due to differences in characteristics of the materials (strongly related to design) [2], differences in separation efficiencies (physical constraints) and thermodynamic and kinetic properties and complex interactions between the materials in metallurgical processing as discussed by Reuter et al. [299]. The more detailed definition of the (EU) recycling rate as given in Eq. 7.10 reveals that the actual recycling rate is not a single value, but is determined by a combination of various distributed parameters with each their corresponding standard deviation. This might raise an important discussion, whether it is correct and representative for practice that the EU recycling targets are given as single values, while in fact they should also contain a standard deviation based on the standard deviation and statistics of the various parameters determining this rate. The definition of the recycling rate, being derived by a fundamental description of the resource cycle and recycling system, provides a useful instrument, which reveals the reality and practice of car recycling on a theoretical basis of distributed dynamic parameters and corresponding standard deviation. Therefore this definition and insights could provide a theoretical founded basis for the discussions between automotive industry, recycling industry and the government.

7.5.3 Alternative definitions for the recycling rate

As discussed a generally accepted definition is the one also used by the EU directive, which defines the recycling rate on the basis of the average weight of the car in a certain year of dismantling. To illustrate the importance of a clear and consistent definition of the recycling rate, a few alternatives for defining the recycling rate will be discussed here. However it can also be argued that the recycling rate can be defined over the market/use system by referring it to the input $m^k(t)$. This definition permits the effect of the lifetime distribution of cars to be included as defined by Eq. 7.14. This definition of the recycling rate (Eq. 7.14) describes the recycling rate of cars based on the input and output of the system at a specific moment in time. The lifetime distribution causes the difference between the in- and output of the system.

$$\begin{aligned} \mathrm{RR}_{\mathrm{In-/out\ sys.}}(t) &= \frac{CR \cdot \left(\sum\limits_{k=Al,steel,Cu,plastics,etc.} x^k(t) \cdot Recovery(x^k(t))^k \right)}{\sum\limits_{k=Al,steel,Cu,plastics,etc.} m^k(t)} \\ &\cdot \quad 100\% \end{aligned} \tag{7.14}$$

The recycling rates (RR) as defined in both Eq. 7.10 and Eq. 7.14 refers to the end-of-processing. The recycling rate includes the collection rate as well as the recovery rate, which is determined by physical and metallurgical processing.

Another way of defining the recycling of cars is presented by Eq. 7.15. The recycling is determined by referring it to the accumulated cars in the (market/use) system ($y^k(t)$, Eq. 7.6). Eq. 7.15 describes the recycling of cars based on the recovery with reference to the cars still in the system, which therefore is a valuable measure of the "mine" of materials still on the road available for recycling.

$$Recovery_{System}(t) = \frac{\sum\limits_{k=Al,steel,Cu,plastics,etc.} x^k(t)}{\sum\limits_{k=Al,steel,Cu,plastics,etc.} y^k(t)} \cdot 100\% \tag{7.15}$$

Eq. 7.10 reflects in a much more correct description the definition of the recycling rate as defined in the EU directive on end-of-life vehicles, although it has the same basic definition. The other two definitions (Eq. 7.14 and Eq. 7.15) illustrate that the recycling or recovery rate can also be defined on a totally different basis and are discussed here to illustrate other aspects of the recycling system, and illustrate the sensitivity of the recycling system.

7.5.4 Accuracy of the model

The results derived from the dynamic model are based on the integration of the various defined distribution functions. A numerical integration technique is applied in the model to calculate the various integrals. The accuracy of the model was verified by comparing the results for the average (or first moment) of the distributions derived by the numerical integration in the model with that of the theoretical first moment of the (Weibull) distribution function as defined by Eq. 7.16.

$$\mu_1 = \beta \cdot \Gamma(\alpha^{-1} + 1) \tag{7.16}$$

where

$$\Gamma(n) = \int_{0}^{\infty} e^{-x} x^{n-1} dx$$

7.5.5 Standard deviation/error margin

The output of the dynamic model (e.g. the recycling rate) is subject to the standard deviation around each of the parameters and distribution functions within the model. The standard deviation or error margin around the output of the model is a complex function of:

- Standard deviation of each of the individual data points of the life time, weight and composition of the car; this standard deviation is here determined by the fitting of the data with a Weibull function, by using the least-square fitting method , in which a normal distribution and its corresponding standard deviation are assumed around each individual data point.
- Standard deviation of the various Weibull functions, which is given by the second moment of the Weibull function (Eq. 7.17):

$$\mu_2 = \beta^2 \cdot \Gamma(2\alpha^{-1} + 1) \tag{7.17}$$

where

$$\Gamma(n) = \int_{0}^{\infty} e^{-x} x^{n-1} dx \tag{7.18}$$

7.6 Dynamic simulation of the recycling and recovery rate of cars

The time-varying distributions of the changing lifetime, weight and composition of the car (Figure 7.5, Figure 7.8 and Figure 7.9), defined by changing values for α and β, determine the recycling rate based on the end-of-life weight and composition (Eq. 7.10) the recycling rate over the in-/output of the system (Eq. 7.14) and the recovery rate over the system (Eq. 7.15). Based on four different simulations the influence of each of these distribution functions on the average weight and composition of the car per year of dismantling ($x^k(t)$), being the basis for the recycling rate as defined in EU legislation, will be discussed below by the use of the dynamic model. Furthermore, these dynamic simulations will be applied to illustrate the effect of these changing distributions on the various definitions of the recycling rate of the car ($RR_{EoL}(t)$ and $RR_{In-/outputsystem}(t)$) and the recovery rate over the system ($Recovery_{System}(t)$) over time (Eq. 7.10, Eq. 7.14 and Eq. 7.15) and therefore also demonstrate the difference between the various definitions of the recycling/recovery rate as discussed here.

7.6.1 Definition of the distribution functions for simulation

As discussed Eq. 7.6 has been derived with reference to Figure 7.2. In the simulations the accumulation of cars in the market place or use phase ($y^k(t)$), as well as the in- and output of the system ($m^k(t)$ and $x^k(t)$) are described as a function of t_1=1981 to 2001 and t_2=1981 to 2021. Each weight class 1 to 20 (or 500kg to 2400kg) of distribution function $g(t_1, w)$ is also associated with an element content as defined by the mass percentage distributions

$h^k(w, mp^k, t_1)$. For illustrative purposes the mass percentage classes in the distributions have been defined varying between 0.25% Al, 0.25% Cu and 2% for steel for mass percentage class 1 up to 10% Al, 10% Cu and 80% steel for class 40. The other materials in the car (e.g. stainless steel, zinc, lead, glass, rubber, plastics, etc.) are described together in a mass percentage distribution and are defined as k = rest. For each of the individual weight classes $w = 1$ to 20, a mass percentage distribution has been defined (see Appendix C.1 and C.2). The lifetime, weight and composition distributions of the car are changed by varying the shape and scale of the distribution functions for the different simulations by changing values for α and β. Tables 7.7 and 7.8 give the values for α and β for the four different simulations for $f(t_1, t_2)$, $g(t_1, t_2)$ and $h^k(w, mp^k, t_1)$. The selected values in simulations 1, 3 and 4 for the lifetime distribution $f(t_1, t_2)$ are based on the average lifetime of the car at the year $t_1 = 20$, which is defined as being constant (this is however not the case) and is therefore not describing the real data trend over time. In simulation 2 the definition of the distribution $f(t_1, t_2)$ is based on realistic data for the Netherlands as given by Figures 4.3 and 7.3. The weight distribution $g(t_1, t_2)$ is defined based on the real statistical data defined in Figures 7.6 and 7.7 for simulations 1,2 and 4. In simulation 3, the weight distribution $g(t_1, t_2)$ has been changed to demonstrate the influence of a different weight distribution. The weight distribution is in this simulation based on semi-theoretical values. Since insufficient data on the mass percentage distributions for the different weight classes hk(w,mpk,t1) was available, the mass percentage distribution for all simulations could not be defined based completely on real statistical data. However the defined values and trends are realistic, when comparing them to the data available and make clear their effect. For these calculations the assumption is being made that the production starts at t=0, whereas the simulations are performed over a period of 20 years. The production rate per year for cars is defined constant at $C(t_1) =$ 1,000,000 at the collection rate (CR) is assumed to be 1.

Table 7.7: Definition of variables of distribution functions $f(t_1, t_2)$ and $g(t_1, w)$ for various simulations

	$f(t_1, t_2)$	$g(t_1, w)$
Simulation 1	$\alpha = 6.8$ $\beta = 14$	$\alpha(t_1) = 3.1 + 0.05 \cdot (t_1 - 1)$ $\beta(t_1) = 5.1 + 0.20 \cdot (t_1 - 1)$
Simulation 2	$\alpha(t_1) = 4.7 + 0.10 \cdot (t_1 - 1)$ $\beta(t_1) = 8.3 + 0.30 \cdot (t_1 - 1)$	$\alpha(t_1) = 3.1 + 0.05 \cdot (t_1 - 1)$ $\beta(t_1) = 5.1 + 0.20 \cdot (t_1 - 1)$
Simulation 3	$\alpha = 6.8$ $\beta = 14$	$\alpha(t_1) = 4 + 0.10 \cdot (t_1 - 1)$ $\beta(t_1) = 6 + 0.25 \cdot (t_1 - 1)$
Simulation 4	$\alpha = 6.8$ $\beta = 14$	$\alpha(t_1) = 3.1 + 0.05 \cdot (t_1 - 1)$ $\beta(t_1) = 5.1 + 0.20 \cdot (t_1 - 1)$

The mass percentage distribution of the remainder (rest) $h^{rest}(w, mp^{rest}, t_1)$ for the various weight classes of the car is derived from the distributions of aluminium, steel, and copper, since the total mass percentage of all the components k must be 100 (see Eq. 7.6).

Simulation 1

Simulation 1 is the basis for all the other simulations. In this simulation, the lifetime of the cars is kept constant over time (with an average of 13.1 years). The weight at production is increasing from an average of 856 kg in year 1 (1981) to 1207 kg in year 20 (2001), and is defined as a linear function of the year of production. The weight distribution as defined

Table 7.8: Definition of variables of distribution function $h^k(w, mp^k, t_1)$ for various simulations

	$h^{Al}(w, mp^{Al}, t_1)$	$h^{steel}(w, mp^{steel}, t_1)$	$h^{Cu}(w, mp^{Cu}, t_1)$
Simulation 1	$\alpha(w) = 5 + 4 \cdot (w/40)$ $\beta(w) = 6 + 2 \cdot (w/40)$	$\alpha(w) = 30 - 5 \cdot (w/40)$ $\beta(w) = 75 - 30 \cdot (w/40)$	$\alpha(w) = 6 - 2 \cdot (w/40)$ $\beta(w) = 6 - 1 \cdot (w/40)$
Simulation 2	$\alpha(w) = 5 + 4 \cdot (w/40)$ $\beta(w) = 6 + 2 \cdot (w/40)$	$\alpha(w) = 30 - 5 \cdot (w/40)$ $\beta(w) = 75 - 30 \cdot (w/40)$	$\alpha(w) = 6 - 2 \cdot (w/40)$ $\beta(w) = 6 - 1 \cdot (w/40)$
Simulation 3	$\alpha(w) = 5 + 4 \cdot (w/40)$ $\beta(w) = 6 + 2 \cdot (w/40)$	$\alpha(w) = 30 - 5 \cdot (w/40)$ $\beta(w) = 75 - 30 \cdot (w/40)$	$\alpha(w) = 6 - 2 \cdot (w/40)$ $\beta(w) = 6 - 1 \cdot (w/40)$
Simulation 4	$\alpha(w, t_1) = 5 + 4 \cdot (w/40) + 2 \cdot (t_1 - 1)$ $\beta(w, t_1) = 6 + 2 \cdot (w/40) + 0.08 \cdot (t_1 - 1)$	$\alpha(w, t_1) = 30 - 5 \cdot (w/40) - 0.5 \cdot (t_1 - 1)$ $\beta(w, t_1) = 75 - 30 \cdot (w/40) - 0.5 \cdot (t_1 - 1)$	$\alpha(w, t_1) = 6 - 2 \cdot (w/40) - 0.01 \cdot (t_1 - 1)$ $\beta(w, t_1) = 6 - 1 \cdot (w/40) - 0.01 \cdot (t_1 - 1)$

cannot be defined as being constant, but must change over time in order to illustrate the effect of the changing distributions in the next simulations, since with a constant weight over time, no effects can be illustrated (the weight at dismantling will remain constant). Furthermore the composition (for aluminium, steel, copper and rest) is kept constant over time, but differs for each of the weight classes (with an average composition of 5.5% Al. 71.2% steel, 5.4% copper and 17.9% rest for weight class 1 (500 kg) and 6.2% Al, 60.8% steel, 5.0% copper and 28.0% rest for weight class 8 (1200 kg)). In order to illustrate the effect of each individual distribution on $x^k(t)$, $m^k(t)$ and $y^k(t)$ and in this way on the three definitions of the recycling/recovery rate of the car, in each of the three following simulations only one of the distribution functions is changed, while the others remain the same as in simulation 1 (see Tables 7.7 and 7.8).

Simulation 2

The lifetime distribution is changed in simulation 2 in order to illustrate the influence of the this distribution on the weight and composition of the car at dismantling ($x^k(t)$) and hence on the defined recycling/recovery rates (Eqs. 7.10 to 7.15). In simulation 2 the average lifetime of the car is increasing over time from 7.6 years at $t_1 = 1$ (=1981) to 13.1 years at $t_1 = 20$ (=2001) based on a lifetime distribution for each production year. This changing lifetime distribution is based on the extrapolated data of Figures 4.3 and 7.3.

Simulation 3

Simulation 3 depicts the influence of the weight distribution (increased weight in comparison to simulation 1) on the weight and composition of the car at dismantling and hence on Eq. 7.10 to Eq. 7.15.

Simulation 4

Simulation 4 illustrates the effect of the changing distribution of the mass percentage over time. In this simulation, the mass percentage for each of the different weight classes is changing over time. The mass percentages of aluminium and rest are increasing, while at the same time the mass percentages of steel and copper are decreasing, following the trend as defined in Table 7.6.

7.6.2 The weight and composition of the average car at recycling

The distributions of the changing lifetime, weight and composition at production determine the weight and composition of the car at a specific moment in time (dismantling year) and are an integrated part of the different definitions of the recycling and recovery rate of the car (see Eq. 7.10, Eq. 7.14 and Eq. 7.16). Figure 7.10, Figure 7.11 and Figure 7.12 illustrate the effect of the various distributions on the weight and composition of the car ($x^k(t)$). It is clear that these results indicate a non-linear relationship between t_2 (year of dismantling) and the variables defined on the y-axes of the different graphs (Figure 7.10, Figure 7.11 and Figure 7.12) as a function of α and β.

Simulation 1

Simulation 1 shows the weight and composition of the car at dismantling for the defined distributions, being the basis for comparison for the other simulations. In spite of an increasing car weight over time with an average of 856 kg for the year of production 1 to 1207 kg for year

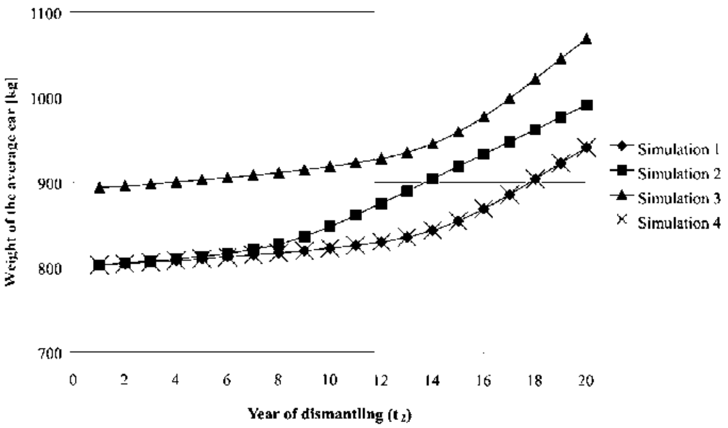

Figure 7.10: Weight of the average car $x(t)/N(t)$ at dismantling as a function of the year of dismantling t_2 for simulation 1 to 4

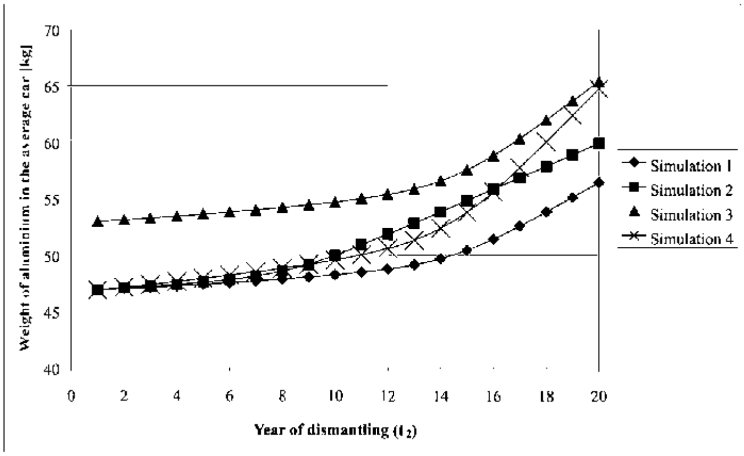

Figure 7.11: Weight $x^{A}l(t)/N(t)$ of aluminium in the average car at dismantling $(x(t)/N(t))$ as a function of the year of dismantling t_2 for simulation 1 to 4

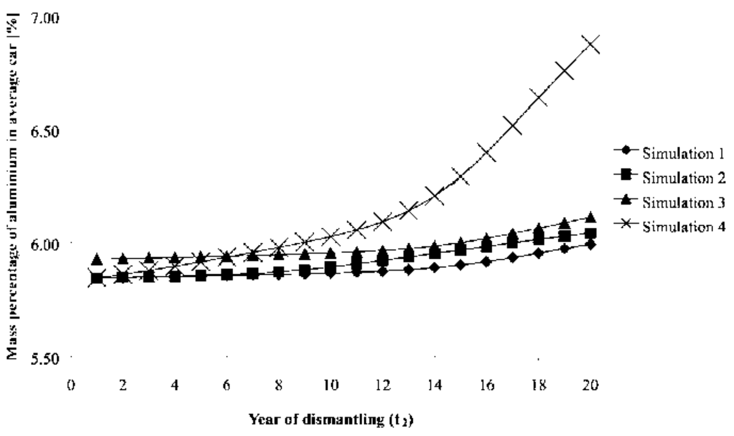

Figure 7.12: Mass percentage of aluminium in the average car at dismantling $(x^{Al}(t)/x(t))$ as a function of the year of dismantling t_2 for simulation 1 to 4

20, the average weight of the car available for recycling from dismantling year 1 to 20 only reaches a value between 841 kg to 941 kg for this simulation due to the delay in the system (lifetime distribution). The same applies for the composition of the car.

Simulation 2

The second simulation clearly illustrates the consequences of a changing lifetime of the car. With an increasing lifetime of 7.6 years in YP=1 to 13.1 years in YP=20 as defined for simulation 2, the weight of the car at dismantling is over time higher than in simulation 1, but still lies between 802 kg (YD=1) to 991 kg (YD=20) (Figure 7.10). The same trend applies for the weight of the components in the car (Figure 7.11). It becomes apparent that there is a significant time delay before the increase in weight of the car and its components at production are visible at dismantling in simulation 1 and 2, however in simulation 2 the weight increases faster due to the shorter lifetimes of the car in simulation 2 compared to simulation 1 (in simulation 2, the lifetime distribution only reaches the value of the lifetime of simulation 1 in $t_1 = 20$). The weight at dismantling is determined by the weight of the car over a range of production years, returning for recycling according to the lifetime distribution function. Since the ratio between the weight of the car and the weight of aluminium in the car changes, the mass percentage of aluminium in the car at dismantling (composition) for simulation 2 show a small difference to that of simulation 1 (Figure 7.12). The ratio between cars with e.g. a low percentage of aluminium produced in the first production years and the cars with e.g. a higher percentage of aluminium produced in the later production years (due to the increasing weight over time combined with an increasing mass percentage of aluminium for the higher weight classes) is different from simulation 1 and leads to a change in the mass percentage at dismantling.

Simulation 3

The effect of the changing weight distribution on the system is made explicit by simulation 3. It is quite obvious that a change in the weight distribution of the car at production will lead to a change in the weight of the car and its components at dismantling (Figure 7.10 and Figure 7.11). The difference in weight at the time of production and the weight at dismantling is determined by the distributed lifetime of the car as was already illustrated by simulations 1 and 2. The difference in the mass percentage of aluminium for simulation 3 and 1 is caused by a faster increase in the weight of the car in simulation 3, combined with a higher aluminium content for the higher weight classes (Figure 7.12).

Simulation 4

Simulation 4 shows that the weight of aluminium in the average car at dismantling is increasing significantly with an increasing Al-content of the car (Figure 7.11) as defined by the changing distribution over time (Table 7.8). Obviously the mass percentage of aluminium in the car at dismantling is changing simultaneously (Figure 7.12). The difference between both the weight of aluminium and the mass percentage of aluminium in the car at production and dismantling is due to the distributed lifetime, although remaining constant over time. The changing distributions of the mass percentage of the various components in the car have no influence on the total weight of the car at dismantling (Figure 7.10), since the sum of all elements must always be equal to 100%. The changing mass percentage of the components in the car (changing composition of the car at dismantling), as depicted in Figure 7.12 for aluminium, together with the recovery per component will influence directly the recycling rate of cars (Eq. 7.10 and 7.14). This will be discussed in the next sections.

7.6.3 The recycling rate at end-of-life

Eq. 7.10 describes the role of the weight and composition of the car at dismantling ($x^k(t)$) in the definition of the recycling rate. Combined with the recovery for each of the different components in the car and the collection rate of cars (Eq. 7.10), the recycling rate RR_{EoL} can be calculated over time. Figure 7.13 shows the effect of the various distributions on the recycling rate, based on the four defined simulations.

Figure 7.13 shows that a change in the lifetime, as well as in the weight or composition of the car at the input (=production) as defined for the various simulations (Tables 7.7 and 7.8) will result in a change in the recycling rate to be achieved. Figure 7.13 clearly illustrates that the recycling rate of the car as defined by Eq. 7.10 is influenced by each of the discussed distributions. It must be noted that the RR_{EoL} for all simulations starts at a value lower than 100%, since the recovery rate for each of the materials will always be lower than 100% as discussed. The RR_{EoL} is determined by the average weight of the components in the car at dismantling combined with the recovery per component (Eq. 7.10). The average car in dismantling year 1 consist of 5.9% Al, 66.0% steel, 5.2% copper and 22.9% rest for simulations 1,2 and 4. These values multiplied with the recoveries per component as given in the caption of Figure 7.13 result in a recycling rate of only 72.6% as a starting value. For simulation 3 the recycling rate even starts at a lower point, since the weight distribution is defined differently, resulting in a different composition of the car at dismantling (see Figure 7.11 at YD=1). It must be mentioned that the simulations presented here do not intend to calculate the real value for the recycling rate of the car being achieved in Europe at this moment. The recovery values given in the figure caption (Figure 7.13) are estimated values in order to illustrate the effect of the various distributions combined with the collection rate and the individual recovery

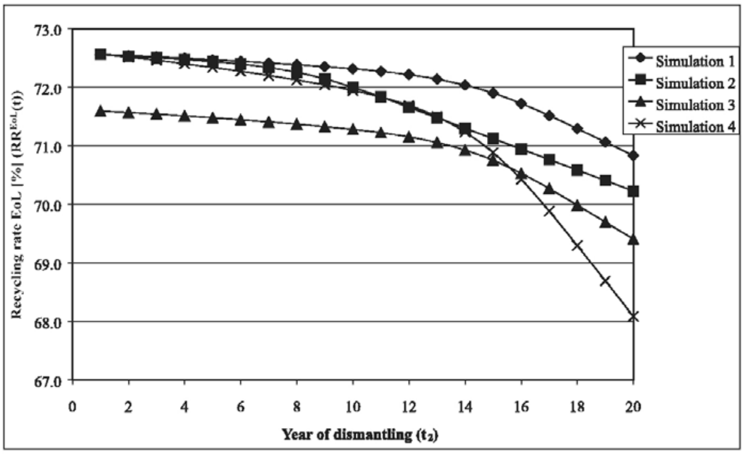

Figure 7.13: Recycling rate ($RR_{EoL}(t)$, Eq. 7.10) of the car as a function of the year of dismantling t_2 for simulation 1 to 4 (CR=1, $RecoveryAl$ = 0.75, $RecoverySteel$ = 0.95, $RecoveryCopper$ = 0.60 and $RecoveryRest$ = 0.10, all constant over time)

rate of the components on the recycling of the car. These recovery values for the different components must be determined carefully since they are also subject to various parameters as discussed by Van Schaik et al. [51, 6]. The calculation of the recovery rate within in the dynamic resource cycle and recycling system will be discussed in detail in the next Chapter 8, since the recovery rate is complex to determine and is dependent on e.g. the available recycling technology, the efficiency of the different processes for mechanical and metallurgical recycling, the optimal arrangement of the recycling flow sheet, as well as the characteristics of the materials in the car and their complex interactions. The changing recovery of the various components in the car is not taken into consideration in the recovery values as given in the figure caption (Figure 7.13). However the dynamic model and the derived definitions can easily handle time dependent recovery values as will be discussed in the next Chapter. This would lead to even more complex changes in the recycling rate over time. It is however of utmost importance to be aware of the effect of these time-varying parameters on the changes in the recycling rate. This complex resource cycle system can only be properly analysed using the definition of the recycling rate based on a dynamic model and the defined distributions.

Simulation 1

As before, simulation 1 is the basis for the other simulations. The recycling rate is decreasing over time for this simulation, since the heavier cars with a lower recoverability are produced in the later years and will become available for recycling later in time (for the heavier cars, the weight distribution is shifted to the high weight classes, which contain more aluminium, which has a recovery of 0.75, more rest, which has a recovery of 0.10 and less steel, with a recovery of 0.95 (i.e. 95

Simulation 2

In simulation 2, the recycling rate has a lower value than for simulation 1. Due to the decreased lifetime, the decrease in recycling rate for the heavier cars will become visible earlier than in simulation 1 at dismantling time.

Simulation 3

Simulation 3 shows the effect of the changing weight distributions on the recycling rate over time. The recovery is decreasing due to the increasing weight of the car, with a lower recoverability due to the defined mass percentage distributions and recovery for the different elements (see also Figure 7.10 and Figure 7.11).

Simulation 4

In simulation 4, the mass percentage distributions for the different elements are changed over time (increasing content of aluminium, and rest (=e.g. plastics), and decreasing content of steel and copper, which means a lower recovery for the car). As expected, the recycling rate decreases significantly for simulation 4 due to the changed mass percentage distributions. It becomes clear that e.g. a higher content of plastics in the car (this implies that α and β of the mass percentage distribution for plastics are changed to give a skew function to the high mass percentage classes) will result in a lower recycling rate, since the recovery of plastics is lower than that of metals. This effect however only becomes apparent after a longer period of time due to the delay in the system caused by the lifetime distribution (see Figure 7.13).

Summary of simulations

It is clear from these simulations that a change in one or more of the distributions will not only lead to changes in the weight and composition of the car at dismantling ($x^k(t)$), but will also result in a change in the total amount of recovered materials from it (due to different recoveries for the various elements) and lead hence to a difference in the recycling rate as depicted by Figure 7.13.

7.6.4 Recycling rate over the in-/output of the system

Another basis for the definition of the recycling rate of the car is defined by Eq. 7.14. The recycling rate is defined here referring the recovery of the output $x^k(t)$ of the system to the input mk(t) of the system. This definition of the recycling rate includes the difference in the total weight of the car and corresponding components produced at a specific moment in time and the total weight of the car and corresponding components recovered at that moment at dismantling. This difference in in- and output of the system at a certain time t is caused by the delay in the system (use phase) due to the lifetime of the car.

Based on the simulations as defined in Tables 7.7 and 7.8, the effect on the various distributions on the recycling rate over the in- and output of the use phase (system) as defined in Eq. 7.14 is depicted by Figure 7.14. The recycling rate increases significantly over the first period, since the weight of the cars flowing out of the system per year increases from the year of dismantling 1 according to the lifetime distribution (Figure 7.4) of the car. The influence of the lifetime is clearly illustrated by the second simulation. The recycling rate is for this situation higher compared to simulation 1, due to the decreased 'residence time' of the cars in the system leading to a higher total amount cars and corresponding weight ($x^k(t)$) flowing out of the system. The influence of the changing weight and composition of the car

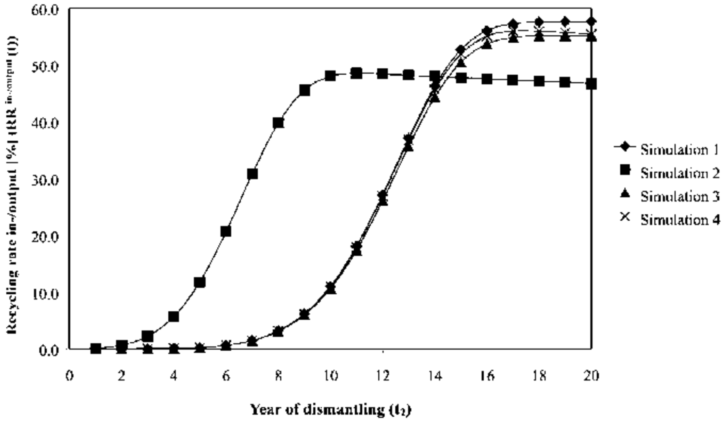

Figure 7.14: Recycling rate over in- and output of system ($RR_{In\ \ /output\ system}(t)$) as a function of the year of dismantling t_2 for simulation 1 to 4

over time, resulting in a decreasing percentage of recycled materials over time (Figure 7.13) causes the decrease in the recycling rate after a certain simulation period, which is clearly visible from the results in Figure 7.14 for simulation 2. This explains why the recycling rate of simulation 2 becomes lower than the recycling rate of simulation 1 at about $t_2 = 14$. The different influences of the changing weight and mass percentage distributions become clear from the difference in recycling rate for the simulations 1, 3 and 4.

7.6.5 Recovery rate over the system

The dynamic model was originally developed to calculate the amount of material locked up in the system $y^k(t)$ determined by solving Eq. 7.6. The total number and weight of cars available for recycling plays a significant role in the realisation of the recycling targets as imposed by EU directive by influencing the economy of the resource cycle. The logistics of the car cycle, the potential of the market to absorb materials (e.g. market saturation for secondary plastics), and the economy of scale for the recycling processes, to name a few, are highly dependent on the number of cars and the total amount of materials leaving the use phase each year. The weight and amount of cars available for recycling in relation to the accumulated (locked up) material in the use/phase is defined by Eq. 7.15 and is defined as the recovery rate of cars from the system. The outflow of cars from the system, becoming available for recycling over time, in relation to the cars accumulated in the system is described by the recovery over the system. Figure 7.15 illustrates the effect of a change in the various distributions on the ratio between the total weight of cars becoming available for recycling over time ($x^k(t)$) and the weight of the cars/material locked up in the system ($y^k(t)$), giving the recovery rate over the system ($Recovery_{system}(t)$). The same variations in the variables were used as in the other simulations. Figure 7.15 shows that due to the lifetime of the car, the weight of cars and corresponding materials remaining in the system $y^k(t)$ compared to the weight of cars and corresponding materials leaving the system $x^k(t)$ is high and results in a low recovery over the system. For simulation 2, the recovery is higher, since the lifetime distribution is shifted here to lower values. It takes less time before the cars will flow out of

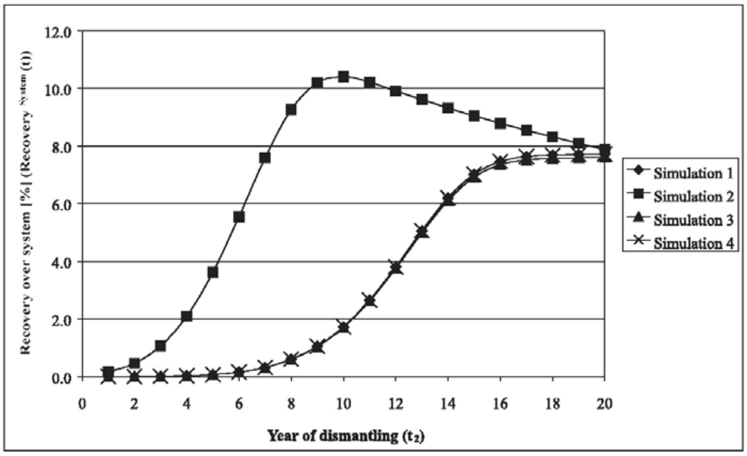

Figure 7.15: Recovery rate over system ($Recovery_{system}(t)$) as a function of the year of dismantling t_2 for simulation 1 to 4

the system. The simulations have to be carried out over a longer period of time before the recovery over the system will increase. The decrease in recovery halfway the simulation period of simulation 2 is caused by the increasing weight of the car over time flowing into the system in combination with the outflow of the lighter cars (produced in the first production years). This is influenced by the increasing lifetime of the car. Simulation 1 and 4 are giving the same results since the change in the mass percentage distribution does not affect the total weight of the cars in the system (the sum of all component is always 100%). Since the recovery over the system is determined based on the total weight of the cars, a change in the mass percentage distributions of the different components will have no effect on the recovery over the system. The small difference in the recovery over the system for simulation 3 (especially in the higher years) compared to case 1 and 4 (recovery for simulation 3 is slightly lower) is caused by the increasing weight of the car at production combined with the lifetime distribution of the car. The difference in weight between the produced cars over time is higher in simulation 3. Combined with the defined lifetime distribution, this results in the accumulation of heavier cars in the system, whereas a higher amount of lighter cars (from the first production years) are leaving the system.

Summary of simulations

Simulations 2 to 4 only show the effect of one changing distribution, compared to a base case scenario (simulation 1). In the reality, all three distributions as well as the defined recovery values for the various materials (figure caption Figure 7.13) are changing simultaneously, which will lead to major changes in the weight and composition of the car (combined output of simulation 2 to 4), and its recycling and recovery rate over time. It becomes clear from the simulations that, in order to describe and quantify the behaviour of the recycling rate (e.g. for EU legislation), it is fundamental to use the dynamic modelling as a basis for the definitions of the recycling rate. The detailed knowledge of the complex interactions between product design, liberation, mechanical separation efficiency and pyro- and hydrometallurgical processing to close the material cycle being an integrated part of this dynamic model is indispensable to fully understand the implications of changing product design on recycling legislation over time. The discussion of EU recycling policy and the determination of the recycling rate requires proper knowledge on the behaviour of the recycling system over time, caused by the complex interactions of the changing distributions. This insight could never be attained by qualitative predictions or calculations based on single or average values for the lifetime, weight and composition of the car. This could even lead to incorrectly calculated recycling values and predictions on the recycling rate, due to the complex interactions within the recycling system, which cannot be understood based on average value calculations, as is required by the simple definition of the recycling rate in the EU legislation.

7.7 Examples and case study

7.7.1 Building waste

In a building an inventory of 150 t of aluminium is identified. Then the building is demolished and 145 t of the identified aluminium goods are inspected to end up as scrap in containers for delivery to metal/scrap traders. Later at a refiner a sample melt results in a metal yield of 85%, or about 87% metal content. The recycling rate would then be (145/150)×0.87 = 84%, regardless of the time of production of these aluminium goods. [48]

7.7.2 Recycling of Al from buildings

A building contains 180 t of aluminium alloys as metal. The collection rate is 95% of the inventory. All subsequent scrap processing plants together deliver 140 t to a refiner. The plant yield of the refiner is 91%.

CR = 0.95 PY = 140/(180 × 0.95) = 0.819 MY = 0.91 RR = 0.95 × 0.819 × 0.91 = 0.708 or 70.8 %.

This implies that 127 t metals are produced out of the initial 180 t of scrap inventory. As nothing is known about the metal content of that scrap inventory the recovery rate can only be assessed: The metal content of the scrap inventory may reasonably be between 90 and 95%, then the recovery rate will be between 127/(180 × 0.95) − 0.743 and 127/(180 × 0.9) − 0.784, i.e. 74 and 78%.

7.7.3 Is 95% recovery rate for ELV's a "Perpetuum mobile"?

Is 95% recovery rate for ELV's a "Perpetuum mobile"?

In 2015 EU legislation dictates that 95% of an ELV must be recoverable of which 85% must be reused. The questions that can be asked: "Do natural laws permit the legal law of 95% recovery rate to be reached? Or is it a fallacy such as the "perpetuum mobile", which the second law of thermodynamics dictates will never be designed?"

Answer

Recognizing that a commercial recycling system never creates pure material streams, never achieves 100% material recovery during physical separation (dictated by separation physics), never achieves 100% material recovery during high temperature metal production (dictated by thermodynamics) and never achieves 100% energy recovery (dictated by thermodynamics) it is possible to show the following.

The distribution of a material "i" over the complete system can be represented by a normalized linear Quality distribution function as a function of material Quality between 0 and 1 (1 meaning pure material):

$$\text{Normalized quality distribution}_i = \left(\frac{2}{2-\text{m}}\right)[\text{m}_i \cdot \text{Quality}_i + (1-\text{m}_i)] \quad \text{for material i}$$

where

$\text{Quality}_i=1$ is a pure material i

m_i=Distribution shape parameter: $m_i=0$ means square distribution, and $m>0$ ever increasing triangular

The recovery of a material i over the complete recycling system can be realistically described in terms of a linear function of Quality in the feed to the separators, metallurgical reactors and energy recovery units:

$$\text{Recovery}_i = \text{R}_i \cdot [(1-\text{k}_i) \cdot \text{Quality}_i + \text{k}_i] \quad \text{for material i}$$

where:

Quality_i always >0 for all i

k_i = Separation efficiency: $k_i=1$ a recovery of $R_i x100\%$ for all Quality_i

R_i = Maximum recovery dictated by thermodynamics during metallurgy and energy recovery

Summing (integrating) the product of the above two equations over all Quality (assuming that all Qualities can be economically recycled , which is obviously not true) the total Recycling rate for material i becomes as an upper limit:

$$\text{Recovery rate}_i = R_i \cdot \left(\frac{2}{2-m_i}\right) \cdot \left(1 + \frac{m_i \cdot (1-k_i)}{3} - \frac{(1-k_i)}{2} - \frac{m_i}{2}\right) \quad \text{for material i}$$

It is clear from the above equation that the recovery of a material can quickly dip below 95% due to the natural physical and chemistry laws that govern Separation efficiency, Quality and Thermodynamics respectively. This becomes significantly worse if for economic reasons (obvious!) if the feed to the reactors always has a larger value than zero. Furthermore, one has to sum over all materials, to obtain the final result, which could lower the recovery even more.

$$\text{Total Recovery Rate} = \sum_{\text{i=1}}^{\text{N=all materials}} \frac{\text{Recycling rate}_i}{\text{N}}$$

In summary the above concisely illustrates that (i) the Quality distribution and therefore the quality of recycle streams, and (ii) separation and metallurgical recovery significantly affect the recovery rate of materials in any recycling system if considered simultaneously. Note, that economic value of the different material qualities, which dictates quality fed to the reactors, has a further negative impact since equation (3) was derived assuming that everything can be recovered! Furthermore, a common fundamental metric as suggested above, with appropriate sampling and data statistics (and therefore distributions) to monitor the total recycling system, is required at least to legally support the imposed 95% recycling rates.

7.7.4 Evaluate the EU recycling definition

The EU definition for the recycling of cars is given by the following relationship:

$$\mathrm{RR_{EoL}(t)} = \frac{\text{average weight of recycled/recovered material per vehicle and year}}{\text{average weight per vehicle and year}} \cdot 100\%$$

Discuss with reasons the validity of this relationship by referring to the various aspects that affect the material recycling within the car. Refer to the Gamma distribution given below to argue your case.

7.7.5 Calculate recycling rate (I)

For a specific year the distribution of the mass (kg) of cars returned for recycling can be described by a gamma distribution (see function given below) for which α =110 and β=9.5.

$$f(x,\alpha,\beta) = \tfrac{1}{\beta^{\alpha}\cdot\Gamma(\alpha)} x^{\alpha-1} e^{-\frac{x}{\beta}}$$
and
$$\Gamma(\alpha) = \int\limits_0^{\infty} e^{-u} u^{\alpha-1} du$$
$$\Gamma(\alpha+1) = \alpha \cdot \Gamma(\alpha)$$

Furthermore, the distributions of aluminium cast, aluminium wrought, steel, copper and plastics (% in car) within this specific year for an average vehicle are being described by the gamma distributions as given bellow:

$$f_{Al\,cast}(x,\alpha,\beta) = \frac{1}{\beta^3\Gamma(3)} x^2 e^{-\frac{x}{2}}$$

$$f_{Al\,wrought}(x,\alpha.\beta) = \frac{1}{\beta^2\Gamma(2)} x e^{-\frac{x}{2}}$$

$$f_{Steel}(x.\alpha,\beta) = \frac{1}{\beta^{10}\Gamma(10)} x^9 e^{-\frac{x}{7}}$$

$$f_{Copper}(x,\alpha,\beta) = \frac{1}{\beta^4\Gamma(4)} x^3 e^{-\frac{x}{2}}$$

$$f_{Plastics}(x,\alpha.\beta) = \frac{1}{\beta^4\Gamma(4)} x^3 e^{-\frac{x}{3}}$$

Calculate:

- the average weight (kg) of a car.
- the recycling rate of this vehicle (%) based on the data given. Please give arguments for all the assumptions you made to calculate this.

Solution

Answer

This question is easy to solve if one realizes that the average of a Weibull function is given by $\alpha \cdot \beta$ making the average mass of the car 1045kg.
From the given distribution functions its is clear that the average Al(cast)=6%, Al(wrought)=4%, Steel=70%, Copper=8% and Plastics=12%. From this, assuming certain metallurgical recoveries, the overall recovery of material can be calculated.

7.7.6 Calculate recycling rate (II)

The life time distribution , describing the distributed life time of the car for each production year t, is defined by the following parameters (Weibull distribution function).

- $\alpha = 6$
- $\beta = 13$
- t = life time (0,1,2...40) for each year of production

Weibull distribution function:

$$f(t,\alpha,\beta) = \frac{1}{\beta^{\alpha} \cdot \Gamma(\alpha)} t^{\alpha-1} e^{-\frac{t}{\beta}}$$
and
$$\Gamma(\alpha) = \int_{0}^{\infty} e^{-u} u^{\alpha-1} du$$
$$\Gamma(\alpha+1) = \alpha \cdot \Gamma(\alpha)$$

Calculate the recycling rate for the years of dismantling: 5, 10, 15 and 20:

- Derive from the given life time distribution the distribution function for the individual dismantling years;
- Calculate the recycling rate for each of these years.

Solve this question by using the following data for a car:

- Weight: Weight of car = 1000 kg (constant)
- Production: Number of cars produced/year of production = 10 000 (constant)
- Composition of car
  - Steel (wt.%)=75-(YP-1)
  - Aluminium (wt.%)=5+(YP-1)
  - Copper (wt.%)=10
  - Rest (wt.%)= 100- sum(steel+aluminium+copper)
  - (in which YP=year of production)
- Recovery rates (constant)
  - Recovery (steel)=100%
  - Recovery (Al)=85%
  - Recovery (Cu)=95%
  - Recovery (rest)=10%

7.8 Summary

Recycling is an important factor in order to achieve a sustainable development our society. In Europe targets have been laid down by EU legislation for the recycling rate of end-of-life vehicles to be achieved within the nearby future. These strict recycling targets are one of the driving forces for more awareness on the importance of recycling in the product's life cycle as well as for the optimisation of recycling systems. A solid technological framework is required to discuss and assess the performance of recycling systems, as well as to calculate recycling rates in view of EU legislation.

- Literature survey has indicated that a fundamental technological framework is lacking. No theoretically founded and therefore consistent basis exists in order to describe recycling systems and its parameters and to determine the recycling rate of passenger vehicles or any other product under consideration. The EU definition does not provide any insight into the various parameters playing a role in the achievement of the imposed recycling targets, which is however essential to improve recycling systems and product design in order to fulfil these strict targets and therefore does not provide a solid basis to understand and assess recycling systems.
- The definition of the recycling rate of the car as used in the EU directive on end-of-life vehicles is critically reviewed. It is discussed that the recycling rate cannot be represented by an average or single value as required by EU legislation and the ISO norm, but is largely dependent on the dynamic and distributed nature and therefore the standard deviations of the time-varying lifetime, weight and composition of the car. A dynamic systems model have been developed describing the behaviour of the resource cycle and its dynamic and statistically distributed parameters over time and is used to more precisely define the recycling rate and its parameters.
- The various simulations presented, using the dynamic system model, make clear that the weight and composition of the car at production and dismantling, as well as the materials accumulating in the system, are determined by the different distributions and are highly dependent on changes in these. Hence the simulations show the effect of the distributions for the lifetime, weight and composition on the definitions of the recycling and recovery rate of the car as explored in this paper. Moreover, the simulations clearly illustrate the difference in the recycling rates to be achieved, applying the different definitions for the recycling and recovery rate as presented in this chapter. Although this may be obvious, it emphasises the critical importance of an accurately defined recycling rate and its time-dependent parameters used in EU legislation.
- Without the use of a dynamic knowledge based model, the complex recycling system cannot be described properly and accurate enough to discuss the implications of EU recycling policy and the achievement of EU recycling targets.
- It is indicated that without any statistics involved and the issues and theory discussed in this chapter the ISO norm for recycling rate calculation is really useless.

The significant conclusions of this chapter and the consequences for legislation are summarized by the following:

- if output quotas are to imposed as sharply as is foreseen in the EU directive they should be supported by a physical, thermodynamic and practical basis, otherwise it is questionable if quotas have any legal and technological meaning;

- monitoring the quality of the complete system, which includes the guaranteeing of the statistical integrity of all data of complex material flows, could cause such excessive costs that this would become impractical;

  therefore the calculation of recycling/recovery rate, without the statistical based monitoring of data for the recycling system as a whole, is legally impossible to defend;

- in a well run recycling system all actors and plants will operate their process economically, and therefore implicitly within environmental legislation, ensuring an optimal recycling rate will be achieved within and for the system, which permits the flexibility of each operator within the system to run his operation as best as possible within nature's laws.

Nomenclature

$C(t_1)$	Production rate of cars (cars/year) as a function of year of production
CR	Collection rate
$f(t, \alpha, \beta)$	Weibull distribution function with parameters α and β
$f(t_1, t_2)$	Distribution function of lifetime as a function of Years of production and dismantling
$g(t_1, w)$	Weight distribution as a function of Years of production and weight classes w
$h^k(w, mp^k, t_1)$	Mass percentage distribution as a function of weight classes w, mass percentage mp and years of production for each element i
k	Elements/components in the car (Al, steel, copper, etc.)
μ_1	Average or first moment
μ_2	Standard deviation or second moment
mp^k	Mass percentage class of element k
$m^k(t)$	Production of product (kg) for element k
$N(t)$	Amount of cars available at dismantling
$p^k(t)$	Primary product (kg) for element i
$RR_{EoL}(t)$	Recycling rate of the car at end-of-life (EoL) (%)
$RR_{In-/outputsystem}(t)$	Recycling rate of the car over the in- and output of the system (%)
$Recovery_{system}(t)$	Recovery rate over the system (%)
$Recovery^k$	Recovery of element k
t, t_1, t_2	Year, Year of production and Year of dismantling respectively
w	Weight class
$x^k(t)$	End-of-life product (kg) for element k
$y^k(t)$	Products/cars accumulating in market/use phase for element k
YD	Year of dismantling
YP	Year of production
$\Gamma(n)$	Gamma distribution

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Chapter 8

Dynamic modelling and optimization of the resource cycle of passenger vehicles - a technological framework

The recovery rate of the various materials composing the car is one of the parameters determining the recycling rate. In order to describe and optimise the recycling (rate) of passenger vehicles and to calculate and predict the recycling rate in the design phase of the car, the parameters determining the recovery rate for each of the materials present in the car and its relation to the dynamics of the system have to be fully understood. This is only possible if recycling systems, in which the materials present in the car are recovered, are defined more fundamentally than is the case at present. This requires sound technological knowledge and hence fundamental knowledge that describe the behaviour of materials and processes within the recycling system, also in relation to the changing design of the product and its dynamic and distributed properties. In this chapter, a dynamic and recycling optimization model is developed, which covers dynamic material flows over the complete path of product design and manufacturing, the use-phase, mechanical recycling and metal recovery back to the product. The recycling optimization model predicts the recovery rate of the different materials as a function of product design, efficiency of the different recycling process steps (as a function of grade and recovery), characteristic properties of the material flows, economics and legislation based on a technological framework. Through the development of these fundamental models, the importance of the various parameters playing a role in the achievement of high recycling targets will be revealed, also in relation to product design. Various simulations illustrate the application of the models to determine the recycling rate of the car and the metal and material inventory in the resource cycle. The models provide a fundamental tool, which is essential for the optimization of the recycling of the car, as well as for the calculation and prediction of the recycling rate in the design phase.

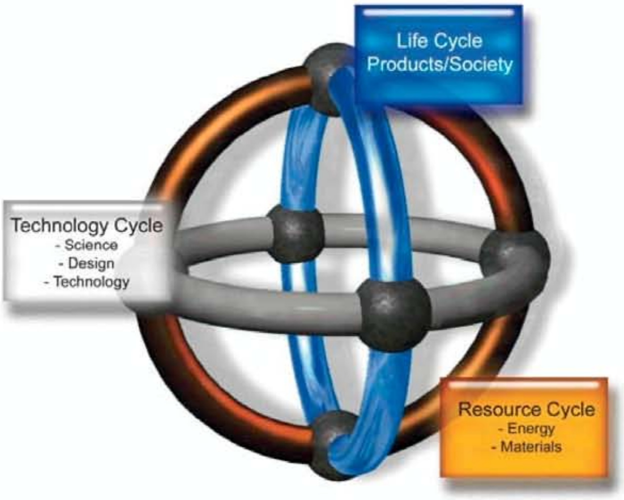


Figure 8.1: Dynamic modelling and optimization of the resource cycle of passenger vehicles - combining the Resource cycle with the Technology cycle

8.1 Recycling rate

The recycling rate of the car has been defined in Chapter 7 as being a dynamic function of the statistically distributed parameters for the design, life time, weight and composition of the car (Eq. 7.6 and Eq. 7.10) as well as of the recovery rate of the different materials composing the car. The recovery rate is highly dependent on the complex interconnected network of mechanical and metallurgical recycling processes in relation to the complex design of the car and the dynamic and distributed nature of the resource cycle. Therefore the recovery rates of the materials present in the car are not single values. In order to describe and optimise the recycling (rate) of passenger vehicles and to calculate and predict the recycling rate in the design phase of the car, the parameters determining the recovery rate for each of the materials present in the car and its relation to the dynamics of the system have to be fully understood. This is only possible if recycling systems, in which the materials present in the car are recovered, are defined more fundamentally than is the case at present. This requires fundamental technological knowledge on the behaviour of materials and processes within the recycling system (Technology cycle, see Figure 8.1), also in relation to the changing design of the product and its dynamic and distributed properties (Resource cycle, see Figure 8.1). Only this will assist in ensuring a sustainable development of our society [50] (Life cycle, see Figure 8.1), in which products have to comply with the recycling targets as imposed by EU legislation [9]. This legislation can only really be implemented if this fundamental knowledge and the tools are available to calculate recovery and recycling rates [2].

In the design of the car various materials are combined and connected in many complex different ways, making up the complex 'mineralogy' of the car and its components, which is changing rapidly and continuously over time. Recycling complex, multi-component products such as passenger vehicles therefore involves:

- a network of interconnected processes (each with their own recoveries, products, residues, etc.) to recover the different materials present in the car (Technology cycle, see Figure 8.1) and;

- material and energy streams (Resource cycle, see Figure 8.1).

The recovery rate of these materials is determined by various aspects like the efficiency of the different unit operations and processes within the interconnected resource cycle system, the characteristics of the materials in relation to the dynamic and statistically distributed design, as well as the optimal interconnection between the different processes in the recycling system. This chapter links the recovery of materials and energy from the various materials present in the car, in other words the Resource cycle of the car with the Technology cycle (see Figure 8.1), which represents the interconnected network of processes as well as the design of the car. Due to these varying conditions a dynamic model has been developed, which covers dynamic material flows over the complete path of product design and manufacturing, the use-phase, mechanical recycling and metal recovery back to the product. The recycling phase is in detail described in a recycling optimization model, which determines the recovery rate and covers in detail the processing of the end-of-life vehicle, starting from dismantling, shredding, and various physical separation steps, including the metal production once again. This chapter discusses the dynamic and recycling optimization model as a theoretical framework to describe and optimise the recycling of cars. The dynamic and recycling optimization model capture the time-dependent recovery of the materials composing the car, as a function of the efficiency of the various processes (physical and metallurgical recycling) composing the flow sheet of the recycling of the car. Through the development of these fundamental models, the importance of the various parameters playing a role in the achievement of high recycling targets will be revealed. The models provide a fundamental tool, which is essential for the optimization of the recycling of the car, as well as for the calculation and prediction of the recycling rate in the design phase as is amongst others required in view of the proposed directive on the type-approval of passenger vehicles. The development of these type of models are essential if design software is to be connected to the recycling of passenger vehicles and design for recycling has to be carried out on a sound technological basis.

8.2 Modelling/simulating the recycling of cars - A theoretical dynamic framework

The resource cycle system can be described at various levels, ranging from the global material cycles; the life cycle system of products; the recycling flow sheet; to e.g. the modelling of liberation in the shredder and optimization of the most complex metallurgical reactor within this recycling flowsheet. Therefore, the optimization of the resource cycle in a world in which products change rapidly is only possible if the interaction between all technological aspects of creating / using / discarding / recycling products is considered in relationship to fundamental studies including environmental control and policy. The aforementioned aspects are summarised into the three cycles depicted by Figure 8.1, symbolically showing the links between three interconnected cycles: the life cycle - the technology cycle - the resource cycle [51]. These simultaneous interactions between the different cycles in Figure 8.1 have to be orchestrated from a systems-engineering point of view, which combines knowledge of processes, production systems and unit operations with that of economics, environment and legislation. It is therefore imperative to achieve sustainability at various system levels, from global material cycles down to plant and process equipment design and operation. Moreover the definition of the recycling rate as well as the role of various parameters playing a role in the realisation of these targets can only be understood if these various system levels are being regarded.

Process synthesis and optimization have been part of process engineering for a long time as illustrated by the papers by Rudd et al. [300], Hendry et al. [301], Hlavacek [302], Nishida et al. [303] and Cisternas [304], as well as by Biegler [305]. Optimization of mineral separation plants, especially flotation plants, has been the topic of various papers [306, 307, 308, 309, 310, 311]. Alexander et al. [312] discusses process synthesis and optimization tools for environmental design applying a multi-objective optimization procedure which makes explicit the trade-offs between environmental, economic and social goals for process design and optimization. Stewart et al. [313] explores the role of Life Cycle Impact Assessment and Environmental Impact Assessment in the evolutionary design of minerals processes on the basis of a hierarchical approach to process design, taking into account linked reactor-separator combinations, as well as complex recycle structures. Also the optimization of large-scale industrial networks for zinc processing, in view of economics and environment, has been studied by Reuter et al. [314] and Sudhölter et al. [129]. In existing literature the recycling of the car is simply described by referring to the different processes and materials involved in the recycling of end-of-life vehicles [37, 38]. In most of these studies recycling is regarded as a combination of de-pollution, selective dismantling and physical separation steps, in which the crucial role of metallurgy is often neglected. No studies were found, which combines a systems approach of the resource cycle with that of recycling, based on a detailed technological knowledge of the complex, statistical and dynamic interactions of recycling systems in relation to the design of the product underpinning in a fundamental manner legislation. Lucas reviews the problems and perspectives in view of ELV regulation in Germany and Europe. In fact, Lucas presents a discussion paper in which an overview of legislation, changing material proportions in ELV's, dismantling strategies is given, as well as the approach of various stakeholders (automobile industry, recycling industry, etc.) to the ELV regulation. A similar type of study has been performed by Wallentowitz et al. [315]. These papers do not give any technological insight into the recycling of end-of-life vehicles and its perspectives in view of the mentioned legislation, making the discussion presented very general and superficial. In order to define the link between end-of-life products, their composition and design a dynamic model was developed for cars [51]. This type of approach has not been used in the recycling field up till now. The architecture of this model as depicted by Figure 8.2 captures the rapidly changing design of products and their role in the material cycle, therefore predicting the input and performance of (future) recycling scenarios and the influence of design on the recycling rate. This model is the basis for the description of car recycling and shows the recycling system embedded in the dynamic material cycle. The two components of the model will be discussed in separate sections. The dynamic model predicts the behaviour of the system in time and as a function of the various involved distribution functions for the life time and composition of the car. The recycling optimization model, describing in detail the recycling system [51], predicts the recovery rate of the different materials in the car as a function of product design, efficiency of the different process steps, characteristic properties of the material flows, economics and legislation. Figure 8.2 reveals that the recycling and recovery rate for the different materials is determined by the dynamic material flows through the resource cycle system.

8.3 Formulation of dynamic model

The dynamic model describes and predicts the behaviour of the resource cycle system as well as the material flows and the accumulation of materials within this system over time as

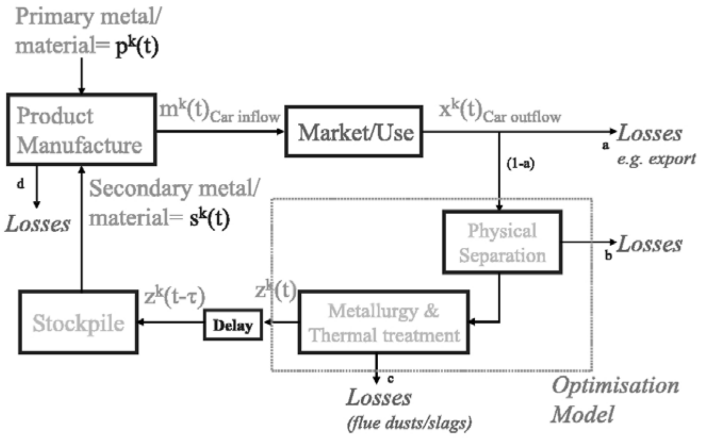


Figure 8.2: The architecture of the dynamic model and the scope of the optimization model for the recycling of cars (a to d are mass fractions between 0 and 1)

depicted by Figure 8.1 [51]. Eq. 8.1 to Eq. 8.4 have been derived with reference to Figure 8.2. Eq. 8.1 describes the accumulation of cars in the market place as a function of the various distribution functions for the life time, weight and composition of the car as defined in the Chapter 7.

$$\frac{dy_1^k(t)}{dt} = m^k(t) - x^k(t) \tag{8.1}$$

where:

$$m^k(t) = \int\limits_{t_1=t}^{t+\Delta t} \int\limits_{w_1}^{w_2} \int\limits_{mp_1^k}^{mp_2^k} C(t_1) \cdot mp^k \cdot h^k(w, mp^k, t_1) \cdot g(t_1, w) dmp^k \cdot dw \cdot dt_1$$

$$x^k(t) = \int\limits_{t_2=t}^{t+\Delta t} \int\limits_{t_1=0}^{YP} \int\limits_{w_1}^{w_2} \int\limits_{mp_1^k}^{mp_2^k} C(t_1) \cdot mp^k \cdot h^k(w, mp^k, t_1) \cdot g(t_1, w) \cdot f(t_1, t_2) \cdot dmp^k \cdot dw \cdot dt_1 \cdot dt_2$$

$$\sum_{k=Al,steel,Cu,plastics,etc.} \int\limits_{mp_1^k}^{mp_2^k} mp^k \cdot h^k(w, mp^k, t_1) \cdot dmp^k = 100$$

Eq. 8.2 describes the accumulation of cars and materials during the recycling operation as described by Figure 8.2. It is assumed that the derivative is equal to zero.

$$\frac{dy_2^k(t)}{dt} = (CR \cdot RR^k) \cdot x^k(t) - z^k(t) = 0 \tag{8.2}$$

The effect of a stockpile is described by Eq. 8.3 in the form of a reservoir controlled by the parameter χ. This equation also makes provision for a delay τ. The stockpile is placed in the flow sheet from Figure 8.2 after the recycling phase, but can be positioned anywhere in the system. Logistics, technological aspects and the influence of market behaviour determine the stockpile. The effect of the delay in the stockpile will be small compared to the influence of the life time of the product.

$$\frac{dy_3^k(t)}{dt} = z^k(t-\tau) - y_3^k(t) \cdot \chi \tag{8.3}$$

Eq. 8.4 defines the mass balance around the manufacture stage. It is assumed that the derivative is zero, which permits the calculation of $p^k(t)$ as a function of the production rate $m^k(t)$ and the recycled material $s^k(t)$. The assumption is being made that all secondary materials coming from the car flow back into the car system. This is obviously not the case for all materials (e.g. steel recycled from cars is being used in the building and construction industry). Using a metal/material cycle approach (instead of a product cycle approach) this can be left out of consideration.

$$\frac{dy_4^k(t)}{dt} = s^k(t) + p^k(t) - m^k(t) = 0 \tag{8.4}$$

where

$$s^k(t) = y_3^k(t) \cdot \chi$$

These equations and distribution functions for the life time, weight and composition of the car have been translated into Matlab®6.1 (see Appendix C.1). These equations can be solved simultaneously by implementing a Runge-Kutta method from Matlab®6.1 as well as suitable numerical integration techniques [235]. By this the composition of the car and the weight of the different components of the car at production and dismantling can be calculated as well as the amount of cars and corresponding material content locked up in the system (see Appendix C.1 for the dynamic model in Matlab®6.1. Melo (1999)[296] discusses that in order to operate a scrap management system successfully reliable methods for predicting metal scrap generation are required. This entails the knowledge of the factors affecting the generation of obsolete scrap. Two of the major factors concern the metal content in manufactured goods sold to end consumers (as is the case for cars as discussed here), and the duration of the products' life time at the end of which disposal occurs and the obsolete metal can be recovered. Melo (1999)[296] mentions that reliable estimates of old scrap generation are of interest not only to the secondary industry, but also to decision makers in the primary industry. For instance, as more metal is recycled, the need for additional smelting capacity in primary production will be lessened. Ayres [316] predicts a decline in the mining and smelting industries in the long term as a result of increasing recycling activities. The emergence of new technologies for reducing scrap into reusable metal, the application of economies of scale to the recycling industries, and the accumulation of large inventories of recyclable metals over time account, among others, for the expected growth in recycling. In spite of the importance of recovering obsolete metal, little quantitative analysis is usually carried out to estimate its reclamation.

8.3.1 Parameterisation of the dynamic model

The statistical nature of the lifetime and design of cars and the modelling of their recycling are discussed in Chapter 7. It is demonstrated that the lifetime, weight and composition of the car are changing over time and can only be described in a proper way by using various distribution functions. These distribution functions determine the dynamics of the system and the input of the recycling operations. The distribution functions for the lifetime ($f(t_1, t_2)$), the weight ($g(t_1, t_2)$) and the composition of the car ($h^k(w, mp^k, t_1)$) are being discussed in Chapter 7 and can be used to parameterise the dynamic model over the total resource cycle as discussed in this chapter as can be read from Eq. 8.1 to Eq. 8.4. Moreover, the (dynamic) recovery rate for the various materials composing the car is to be determined using the recycling optimization model, which describes in detail the recycling system.

8.4 Optimization & Simulation model for recycling end-of-life vehicles

In order to describe, model and optimise the material cycle of passenger vehicles, or any other product or material, it is of critical importance to have insight into the parameters affecting the performance of the system. In this section the development of an optimization model for the recycling of end-of-life vehicles will be discussed.

8.4.1 Technology of recycling - The multi-level flowsheet

The recovery rate of the materials composing the car is determined by state-of-the art recycling technology as well as the arrangement and interconnections between the different recycling processes and the characteristics of the materials to be recycled. End-of-life scenarios of complex multi-component products (such as end-of-life vehicles) consist of a combination of different steps: collection, dismantling, shredding, physical separation, and metallurgical processing of the recovered material streams. Even incineration and land filling can be part of the end-of-life scenarios for a certain product, although land filling and incineration without material or energy recovery are not considered as recycling according to legislation [9], but are however fundamental to include in the recycling flowsheet in order to determine and control losses in the system. The losses within the recycling phase in Figure 8.2 are e.g. caused by increasing product complexity and changing material combinations. Even a small change in product mineralogy (material combinations and connections) due to changing product design can have a significant effect on the final metal recovery and thus on the recycling rate of a product. The final metal recovery is dictated by the prevalent thermodynamics and kinetics of the metallurgical processes, which are the closers of the material cycle [33]. As an example the metallurgical processing of the ferrous fraction coming from end-of-life vehicles illustrates the importance of being capable to express the changing composition of a product at the end-of-life. The maximum concentration of Cu present in the ferrous stream coming from car scrap is restricted to 0.25% [317]. Furthermore the recovery of aluminium is dependent on the purity of the input stream of the metallurgical process, created during mechanical recycling of, in this case, the car. Unacceptable contents of e.g. Cu and Fe require that primary metal is added to achieve the required alloy composition after melting. Losses during melting, due to irrecoverable aluminium oxide, carbide, and sulphide [318] are created as a function of high surface to mass ratios (large surfaces already oxidised), and reaction losses due to aluminium reacting with organic coatings. The complex and multi-component composition of a product results in the distribution of material streams during recycling. Material cycles of complex modern products consist of a network of interconnected processes and material and energy flows. The basis to describe and understand recycling systems is the combination of recycling processes and the material flows within this recycling system being represented by the recycling flowsheet for a specific product or material and its characteristics. As discussed, the resource

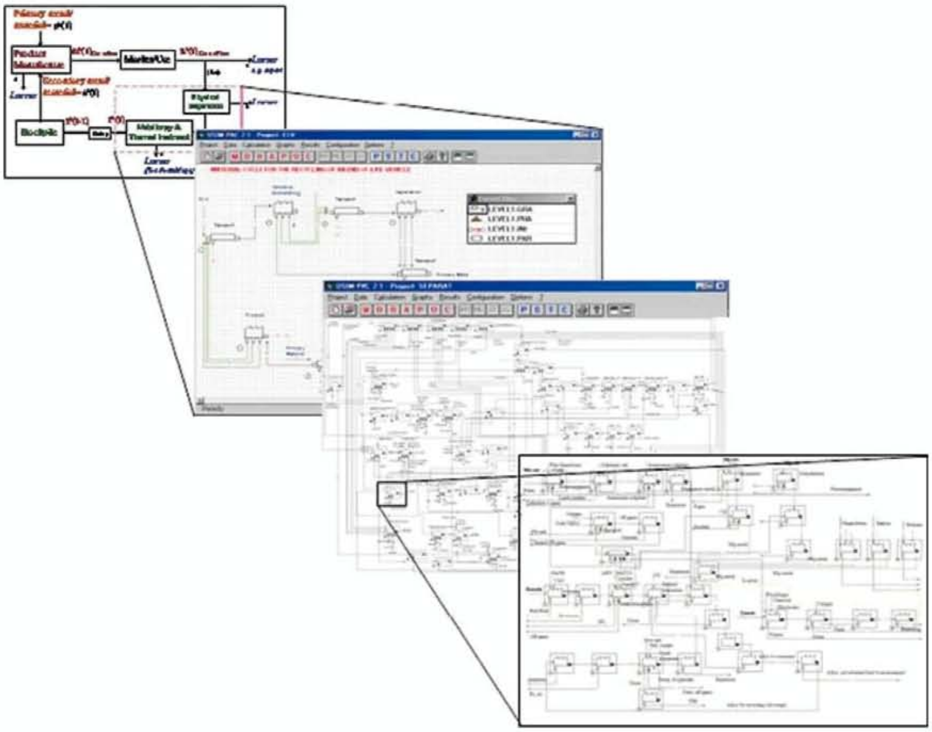


Figure 8.3: Multi-level approach for the description of the interconnected dynamic resource cycle and recycling system of passenger vehicles

cycle and recycling system can be described at various levels, ranging from the resource cycle system of products (see Figure 8.2); a general recycling flow sheet only representing the main operations in recycling end-of-life vehicles (see Figure 1.7); to the detailed description of the network of processes and material flows, which could involve e.g. the modelling of liberation in the shredder and optimization of the most complex metallurgical reactor within this recycling flowsheet. The description and modelling of the resource cycle and recycling system of the car are organised in a multi-level approach as is represented by Figure 8.3.

For the recycling of end-of-life vehicles this complex recycling flowsheet is constructed, showing the technological possibilities of recycling these vehicles. This flowsheet is represented by Figure 8.4 [295, 319, 320, 321, 322] and is developed by the use of the simulation software tool USIM PAC [323]. Figure 8.4 shows the complexity of recycling end-of-life vehicles. This makes clear that recycling ELV's is not just a simple mass balance based on an input stream- the car- and an output stream - the recovered materials, as is often considered by designers, politicians, etc., but involves a network of interconnected processes (each with their own recoveries, products, residues, etc.) and material and energy streams (energy recovery from material flows). Different recycling routes can be followed within the network of processes, depending e.g. on the composition of the (end-of-life) product, which changes with time as determined by the dynamic model (see Chapter 7), the quality of the intermediate recycling streams, the possible applications of the recovered material, the economics of the recycling route and legislation to name a few. Within the resource cycle and complex flowsheet of the recycling system of ELV's, different levels can be distinguished (see Figure 8.3):

- **Level 1** : Figure 8.2 illustrates the resource cycle of passenger vehicles. which not only includes the recycling (physical separation and metallurgy & thermal treatment), but covers the life cycle of the product including production and use.
- **Level 2** : Figure 1.7 gives a simple and very general overview of the recycling flowsheet and depicts the main process steps in recycling end-of-life vehicles.
- **Level 3** : Figure 8.4 depicts a detailed recycling flowsheet, which gives the various dismantling, shredding, mechanical separation and metallurgical and (non-) organics unit operations necessary to recover materials or energy from the car, the architecture of this flowsheet can be changed by adapting the structural parameters of the flowsheet;
- **Level 4** : Figure 1.12 depicts the flowsheet for the recycling and production of aluminium in the simulator, which is connected to the Al-factory (icon 21) in Figure 8.4. Level 4 of the flow sheet gives a detailed description of the different factories as given in Level 3, e.g. metallurgical operations or processing of solid organic materials such as plastics, tires, etc. It is clear from Figure 1.12 that it includes unit operations of primary and secondary aluminium production, not only coming from the car, but bringing together aluminium from various sources, thus showing the interconnectedness of product and metal cycles [7]. This reveals that both primary and secondary processing of aluminium from different sources are part of the recycling chain of the car and affect e.g. the economics. Similar flowsheets can be drawn for the other metallurgical and solid processing plants given in the Level 3 flowsheet (Figure 8.4).

Using this multi-level resource cycle and flowsheet approach makes it possible to keep the top levels as simple and orderly as possible, whereas the sub-layered process flowsheets can be defined in more detail in the third or even fourth level flowsheets. All data on processes and material streams from the bottom level flowsheets are translated to and thus incorporated in the top levels by this multi-layer approach. This is of crucial importance when detailed technological recycling knowledge has to be incorporated into e.g. design for recycling or design for environment strategies or software. The detailed technological knowledge is present in the bottom levels, however the translation to the top levels of the model makes communication to e.g. designers easier, while still maintaining the required technological detail. This multi-level approach also illustrates how the modelling of this work could easily fit into Design for Environment or recycling within the field of Industrial Ecology , as e.g. discussed by [40], which represents a level on top of the ones discussed here. By applying the discussed multi-level approach, even the dynamics of the resource and recycling system can be incorporated into other fields. This multi-level approach has also been applied by Verhoef et al. [7] for the modelling and simulation of interconnected metal cycles.

8.4.2 Interconnected processes and material streams

In addition to technology and legislation, economy and environmental impact also determine the recovery of the material cycle. The developed flowsheet (Figure 8.4; [324]) shows the inseparable relation between the different processes and material flows in the recycling chain. Closing of the material cycle can only be achieved by optimising the mutual compatibility of the successive processes of mechanical recycling and metallurgical operations within this

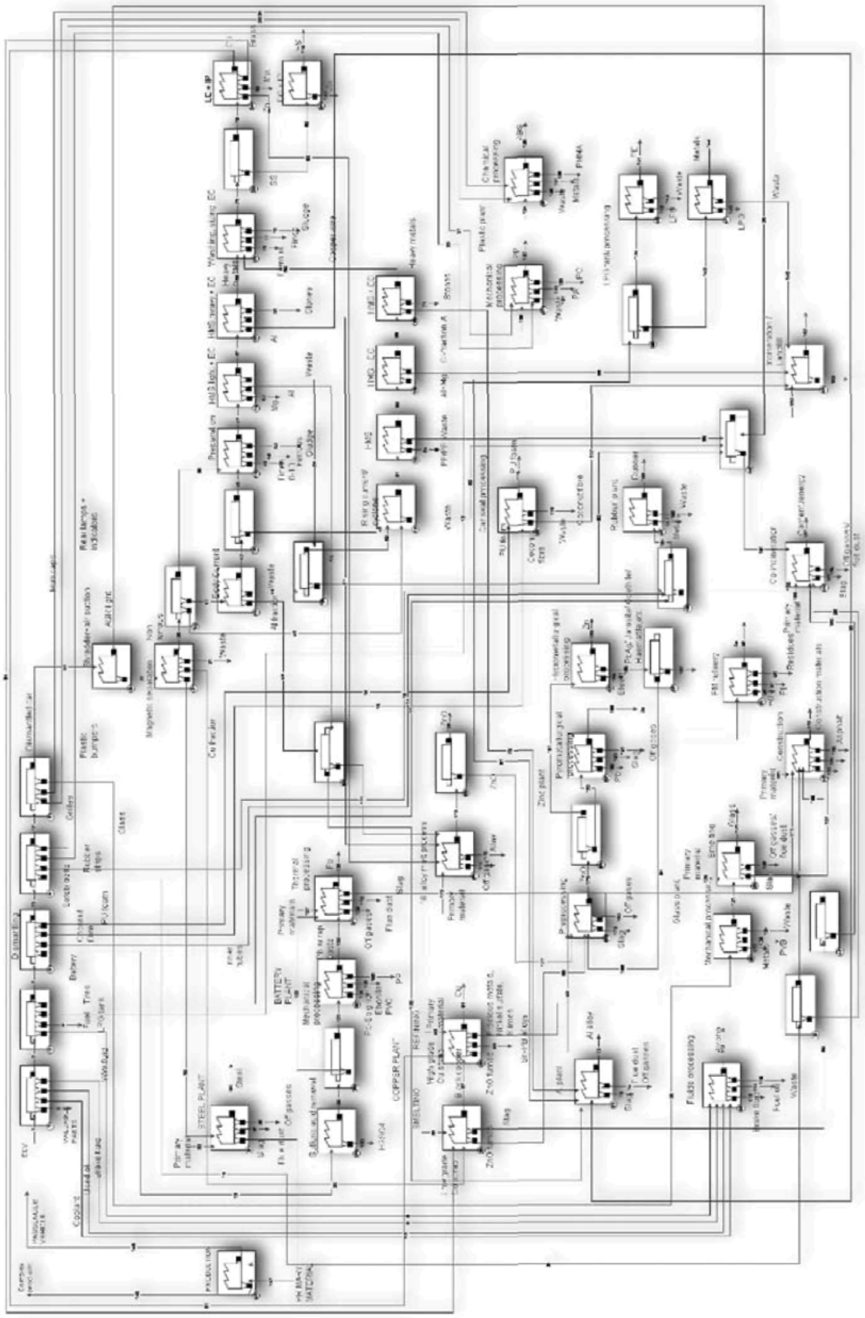


Figure 8.4: Flowsheet of recycling end-of-life vehicles (Level 1) [324]

interconnected resource cycle system. Of critical importance is the quality control of recycling intermediate products created during physical separation, which ensures that the feed to metal producing processes permits the economic production of quality metal products. It is discussed by Verhoef et al. [7] that the dilution of the undesired substances in metals, due to the limited grade of secondary metal flows (recycling intermediate products) through the addition of high-grade primary metals prevents on the long term the closing of material cycles, whereas recovery without dilution reduces the quality (or quantity) of recycled metals. This emphasis the crucial importance of describing and controlling the grade of intermediate recycling products within the recycling optimization models as developed in this Part. Controlling of grade and recovery is presently supported by automated sorting technology [325] to achieve the required product quality for further processing. In addition, the arrangement of the processes within the recycling flowsheet (system architecture), as well as insight into the relation between design and recycling are of major importance to control the quality of intermediate recycling products. The design of the car, being the input of the flowsheet is of direct influence on the efficiency of the various unit operations within the end-of-life scenario of the car and determines the quality of the intermediate recycling products. The varying complex composition of cars with time, as well as the varying lifetimes of the product (which are partly determined by the product design) are determining the recovery rate to be achieved. These complex interactions can only be fully understood and optimised by applying a systems approach to the resource cycle and recycling system.

8.4.3 Definition of the optimization model for recycling end-of-life vehicles

In order to describe, model and optimise the material cycle of passenger vehicles, or any other product or material, it is of critical importance to have insight into the parameters affecting the performance of the system. The description and modelling of recycling systems e.g. for cars, for which the processes and material flows are being defined in the recycling flowsheet of Figure 8.4, requires the knowledge of:

- process characteristics (grade/recovery, process efficiency) of the different types of processes (dismantling, shredding, physical separation, metallurgy, etc.);
- material properties (material types, liberation, etc.);
- critical system parameters (technological, economical and environmental constraints, legislation, etc.);

which are derived from both literature and theory as well as from reliable and detailed industrial data.

Therefore a recycling optimization tool is developed [326, 51], which is able to provide insight into the mutual compatibility of processes and material streams at various stages in the recycling chain, material properties and their relation to the economy, legislation and environmental impact of closing the material cycle. The model will provide transparency into the different factors affecting the recovery rate of the different materials present in the car. The model calculates the recovery rate for the various materials in the car as a function of product design, physical separation efficiency, metallurgy and external constraints such as legislation and economy. This model will be discussed below.

It is evident that the optimization of the material cycle is strongly related to various aspects (to name a few):

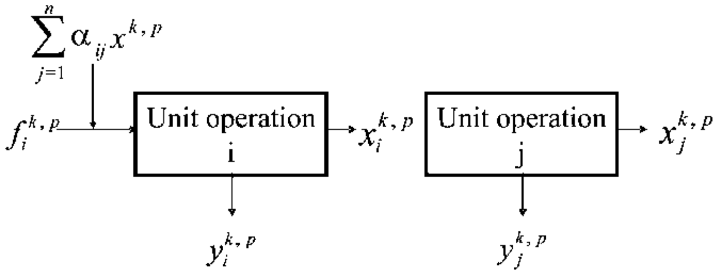


Figure 8.5: General overview of mass flows over unit operation i and j for each element k in a particle size class p

- efficiency of the different unit operations and processes as well as the optimal interconnection between the different processes;
- varying complex composition of cars with time, as well as the varying life-times of the product (given by the dynamic model);
- material quality, type and shape (or particle size) at various stages in the recycling chain, which are determined by product design and technological state-of-the art, and;
- economical, legislative and environmental constraints as well as poorly defined parameters defined by public awareness for example.

These parameters have to be translated into a model in order to describe and optimise the material cycle of passenger vehicles.

Two types of equations can in principal describe the flow of materials in the system of processes and the structure of the network for each individual element, metal or compound present in the car viz.

- mass balance equations, including structural parameters for each element k and particle class p, and;
- separation efficiency models for each of the unit operations i.

The various parameters playing a role in the efficiency of the material cycle (economy, legislation, etc.) are translated into constraints imposed on the model, the equations mentioned and an objective function for optimization. These theoretical equations comprise the basis of the model, giving the constraints imposed on the system. The material flows for elements k in different size classes p between the unit operations and interconnections between these processes as depicted in the recycling flowsheet can be simplified and generalised as shown in Figure 8.5.

The recycling optimization model permits simplification of the complex flowsheet of recycling end-of-life vehicles as given in Figure 8.4. USIM PAC 2.1/3.0 [323] was used to develop the recycling flowsheet [326]. This was not used for the development of the recycling optimization model, since total modelling freedom was required to describe and optimise the car recycling system in its characteristic parameters (e.g. liberation). Therefore the recycling optimization model have been developed using Microsoft® Excel [327] extended with the Large-Scale GRG Non-linear Solver [328] (see Appendix C.3).

Since the process characteristics of shredding, mechanical separation and metallurgical operations are totally different, the model describes the flow of materials in the recycling system for these operations in a different way. The description of these unit operations in the recycling optimization model is discussed below in separate sections.

Formulation of model for shredding

The particle size distribution of the input material is changed during recycling by the shredding operation. The transition of the size classes by the shredding operation is defined in the model by a shredder transformation matrix. This is similar as defined by Reuter and Van Deventer [309].

Mass balance over shredder A mass balance can be set up over the shredding operation, which describes the transition of the mass flow over the particle size classes p for each element k over the in- and output of the shredder (Eq. 8.5 and Eq. 8.6). Since no separation takes place (the in- and output of the shredder are both defined as one stream distributed over the defined particle size classes) no separation efficiency equation for the shredding operation is defined.

$$\left(\sum_{p_f=1}^{p_f=5} Sf_i^{k,p_f,p_y} \cdot f_i^{k,p_f}\right) - y_i^{k,p_y} = 0 \tag{8.5}$$

with

$$\sum_{p_y=1}^{p_y=5} Sf_i^{k,p_f,p_y} = 1 \tag{8.6}$$

Formulation of the model for mechanical separation

Mass balance constraints The mass balance equations define the flow of the material streams between the different unit operations and the structure of the network of processes. A closed mass balance over all unit operations and for all material flows is required to describe any plant or process system under consideration and is therefore essential in modelling the recycling of passenger vehicles as well as to determine the recovery/recycling rate of the car and its components. For the two unit operations i and j as represented in Figure 8.5 the mass balance constraint defined by Figure 8.5 may be derived. Since the performance of the unit operation is obviously related to the feed of the processes, separation equations can be defined for different ranges of input and sizes classes p. For this reason the model describes the material flow for each of the elements k present in the car for different size classes p.

$$f_i^{k,p} + \sum_{j=1}^{n} \alpha_{ij} x_j^{k,p} - x_i^{k,p} - y_i^{k,p} = 0 \tag{8.7}$$

Structure of network The parameter α_{ij}, as given in the mass balance equation is a structural parameter, which determines the flow of the material streams between the different processes as well as the architecture of the flow sheet, and is determined by technology (e.g. input constraints), economics (e.g. transport and process costs), environmental impact (e.g. transport distance, environmental burden of plant), legislation (e.g. restriction on thermal treatment), etc. Eq. 8.8 defines the constraints that apply to the structural parameters.

$$0 \leq \alpha_{ij} \leq 1 \ \text{and} \ \sum_{i=1}^{n} \alpha_{ij} = 1 \ for\, all\, j \tag{8.8}$$

Separation constraints The separation of the feed of each unit operation into different product streams ($x_i^{k,p}$ and $y_i^{k,p}$) can be described by two types of equations, depending on the type of separation and the stream to be described.

Linear relation recovery-grade The mechanical separation of a material can be represented by (non-linear) recovery-grade separation curves. Since the separation process only operates in a specific range of this curve, the curve can be approached within this range by a linear equation as expressed by Eq. 8.9.

$$Ry_i^{k,p} - (a_p \cdot Gy_i^{k,p}) - b_p = 0 \tag{8.9}$$

$$min \leq Ry_i^{k,p} \leq max \ \text{or} \ min \leq Gy_i^{k,p} \leq max$$

where a_p and b_p are parameters determined from plant data and the grade and recovery for each element k in a particle class p defined by Eq. 8.10 and Eq. 8.11.

$$Gy_i^{k,p} = \frac{y_i^{k,p}}{\sum_{k=1}^{n} y_i^{k,p}} \quad \text{grade} \tag{8.10}$$

$$Ry_i^{k,p} = \frac{y_i^{k,p}}{y_i^{k,p} + x_i^{k,p}} \quad \text{recovery} \tag{8.11}$$

The definition of grade in the model constraints gives the possibility to describe the concentration (purity) of an element 'k' in a produced material stream. Since grade is defined as the amount of an element 'k' over the sum of all the other elements 'k', each of them specified by element, it becomes transparent what kind of materials or elements are present in a specific material stream, describing the quality of the materials. As an example the metallurgical processing of the ferrous fraction coming from ELV's illustrates the importance of being capable to express the different types of materials present in a material stream. As discussed above the maximum concentration of Cu present in this stream is restricted to 0.25%. To be able to control and optimise the quality of the processed materials, the model provides this type of data. The translation of the influence of process input (output grade of preceding unit operation) to the efficiency of the metallurgical plant will be discussed below.

Recovery For unit operations or material streams for which description of grade in the separation equation is not functional (e.g. dismantling, residue streams etc.), the separation can very well be described just by the recovery of the process (Eq. 8.12).

$$(1 - Ry_i^{k,p}) \cdot y_i^{k,p} - Ry_i^{k,p} \cdot x_i^{k,p} = 0 \tag{8.12}$$

Formulation of model for metallurgical processing

Mass balance and separation constraints for metallurgical operations The mass balance as well as the separation efficiency (recovery) of the metallurgical operations can in principal be described by Eq. 8.13. The recovery (given by $Ry_i^{k,p}$) can be represented by a fixed value, known from plant experience, or a variable, which is e.g. dependent on the size class p or composition of the input of the process. Since the model focuses in particular on the optimization of aluminium, the metallurgical processing of aluminium is described in the model.

$$\left(f_i^{k,p} + \sum_{j=1}^{n} \alpha_{ij} x_j^{k,p}\right) \cdot Ry_i^{k,p} - y_i^{k,p} = 0 \tag{8.13}$$

Recovery of element k dependent on size class p In recycling of aluminium, the recovery is dependent on the particle size (oxidised surface). Since the model describes the material flow for different size classes p, the recovery values for each of these size classes are defined in the model as fixed values in a matrix.

Recovery dependent on input composition/contamination in input The recovery of aluminium is dependent on the purity of the input stream of the metallurgical process. The presence of organic material in the aluminium fraction will lead to losses during melting [318]. The linear relation defined by Eq. 8.14 can approach the relation of the organic content of the process input and the recovery of aluminium.

$$Ry_i^{k,p} - \left(a_p \cdot Cf_i^{k,p}\right) - b_p = 0 \tag{8.14}$$

In Eq. 8.14 $Cf_i^{k,p}$ is the organic content of the aluminium fraction being the input of the metallurgical process and a_p and b_p are plant parameters (in which b_p is equal to the recovery value for a certain size class p as given in the matrix, which could be obtained from e.g. melting experiments).

Boundary conditions on recycling optimization model

The boundary conditions of the recycling optimization model are given by the technological, economical, environmental and legislative constraints as discussed before and will lead to restrictions on the different variables. An example is the quality of intermediate recycling streams coming from mechanical separation processes, which have to comply with input constraints defined by the metallurgical operation (due to thermodynamics and kinetics). Since the model provides the possibility to calculate the grade (or quality) of each of the material streams, constraints can be put onto the grade of the intermediate recycling streams. The same applies for the output of the metallurgical processes, which have to comply with constraints on the alloy composition. Since each element is described separately in the model, the output of the metallurgical operation can be calculated by adding the different materials present in one stream (in this case, the produced aluminium alloy). Aluminium is described in the model as wrought or cast, each with its own specific (average) composition. To be able to calculate the produced alloy type, the composition of the wrought and cast aluminium is described in a matrix in the model. Together with the contaminants or alloying elements ending up in the alloy, the exact alloy composition can be calculated from the model and can be controlled by defining boundary conditions on the output.

Primary materials (aluminium and alloying elements) often have to be added to produce a required alloy composition. These primary materials are defined as one of the input streams of the model. The addition of primary materials must be kept to a minimum, for economical and environmental reasons. This can be realised by including the primary materials in the objective function for optimization.

Objective function

The objective function, referring to e.g. economics, can be stated as Eq. 8.15, subject to suitable model constraints (determined e.g. by quality, legislation, environmental impact, etc). This function can also be rewritten to include legislative and environmental factors and parameters for optimization (e.g. emissions and energy use of processes, transport, etc. could be related to unit operations and mass flows by expressing them with reference to mass).

$$\begin{aligned} OBJ &= \sum_{i/k} Revenue \cdot \left(\frac{x_i^k}{y_i^k}\right) - \sum_{i/k} Penalties \cdot \left(\frac{x_i^k}{y_i^k}\right) \\ &- \sum_{i/k} Costs \cdot \left(\frac{x_i^k}{y_i^k}\right) \quad \text{(e.g. in US\$/ton)} \end{aligned} \tag{8.15}$$

Statistics of the model

As discussed in Chapter 7 the output of the dynamic model has a standard deviation which is a complex function of the standard deviation of the parameters and distribution functions within the model. The output of the recycling optimization model will also have a standard deviation being a complex function of its numerous parameters. Although the values for the mass and element flows and consequently the grade and recovery are represented in the model as fixed values, these parameters are in fact statistically distributed. Due to the distributed character of the parameters as discussed in Chapter 7 as well as due to plant statistics of the separation efficiency (recovery factors) and grade or quality of the (intermediate) recycling products, the output of the model is subject to a standard deviation, which is a complex function of the standard deviation around the mass/composition of the car (see Chapter 7) as well as the standard deviation of each mass and element flow and therefore the grade and recovery of each individual operation in the recycling flowsheet. Due to the complex dependency of the standard deviation of the output and the standard deviation of the various parameters of the model, this could not easily be determined as such. A Monte Carlo simulation could be performed in which each individual parameter is varied randomly within its error margin, therefore producing the distribution function of the output of the model, from which its standard deviation could be calculated. Due to the lack of properly measured industrial data and its corresponding statistics, this was not done in this work. Van Heukelem et al. [329] used a Monte-Carlo simulation on the modelling of a copper smelter to provide insight into the propagation of variations through the model that predicts the compositions and tonnage of the output for a certain feed composition. The Monte-Carlo simulation uses the results from observed standard deviations from data reconciliation on the copper smelter. The distributions of the assumptions within the model have been set through expert guessing.

Software for optimization

The software application used to perform this optimization is Frontline Systems' Premium Solver Platform, extended with the Large-Scale GRG Non-linear Solver [328], implemented in Microsoft® Excel [327], which is capable of handling these large scale, complex, non-linear optimization problems. Furthermore AMPL was used to solve the problems (See Example in Appendix C.2).

Data collection

Experimental and industrial data on the composition of the car, the efficiency of the various processes, the material stream etc. is essential for the practical use and reliability of the recycling optimization and dynamic model. However, a lot of data on the efficiency of the various processes for the different material streams is lacking, since data collection on recycling systems have not been performed in a systematic and organised manner up till now. A lot of effort is required for people in the recycling field to collect of reliable and statistical representative data. The dynamic and recycling optimization model as developed, together with a detailed definition of the recycling rate provide a solid theoretical basis for the understanding and assessment of recycling systems. The model and definition give a clear structure for the collection of data and corresponding statistics, when performing recycling experiments and assessing recycling systems as well as for the calculation of the recycling rate of the car, or any other product under consideration.

8.5 Optimal dynamic modelling of aluminium recycling - a case study

The dynamic model is creating the input of the recycling optimization model. Recursively the recovery of the different materials present in the car is derived from the recycling optimization model, in which the objective is the optimization of aluminium recycling, given constraints on recovery and grade imposed on the various unit operations described in the recycling optimization model.

8.5.1 Dynamic simulation of the aluminium recycling

The dynamic model was developed describing the recycling of cars as a function of the inflow of cars (i.e. the production rate per year for cars $\dot{C} = 1{,}000{,}000$) minus the outflow of cars defined by the given distribution functions and the area under the curves between two consecutive years (see Figure 7.2 and Figure 7.5). By integrating Eq. 8.1, Eq. 8.2, Eq. 8.3 and Eq. 8.4 from year to year the accumulation of cars in the system can be calculated by the use of Matlab ®6.1 [235]. For these calculations the assumption is being made that the production starts at $t = 0$ which represents year 1981 with other conditions given in the figure caption as well as discussed above. Figure 8.6 gives the lifetime distributions $f(t_1, t_2)$ as used in the simulations for respectively $\alpha = 8$ & $\beta = 10$ and $\alpha = 13$ & $\beta = 5$.

Figure 8.7 and Figure 8.8 clearly show the effect of distributions and recovery rates on the response to the recycling system. Figure 8.8 illustrates the importance for the metallurgical industry to be able to describe the behaviour of the system over time, in order to predict the ratio between primary and secondary metal production. The influence of the time delay on the response to the system (caused by the products lifetime and the delay of a stockpile) is clearly illustrated by Figure 8.8. The recovery rate has a value of 0.5 and 0.9 respectively,

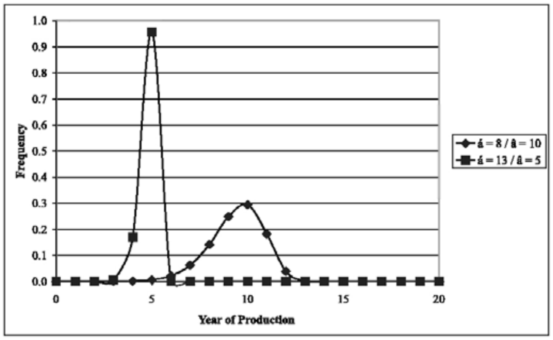


Figure 8.6: Lifetime distribution $f(t_1, t_2)$ for (α =8 & β =10) and (α =13 & β =5)

however the rate of secondary cars i.e. cars applying recycled aluminium in the production only reaches a value of 0.35 and 0.6 after a simulation period of 20 years. The simulation has to be carried out over a longer period of time before the rate of secondary cars finally equals the recovery rate. From the results therefore observe that the recovery rate RR^k eventually determines the amount of secondary material that flows into car production; that it is determined by the length of the simulation, the distribution functions and also by the output of recycling optimization model. The difference between the recovery rate and the rate of secondary materials is also influenced by the changing composition of the car over time. This is so since the feed to the model has been constrained to 1,000,000 cars. The effect of economics, legislation and process efficiency could be integrated into the dynamic model via the recycling optimization model. This model provides values for the decision parameters (b) and (c) as depicted in Figure 8.2 as is discussed in the next section. For example the efficiency of pyrometallurgy (metal yield) will give an estimate for the parameter (c) in Figure 8.2. The input to the recycling optimization model is produced by the intermediate results of the dynamic model (the value $x(t)$, see Figure 8.2).

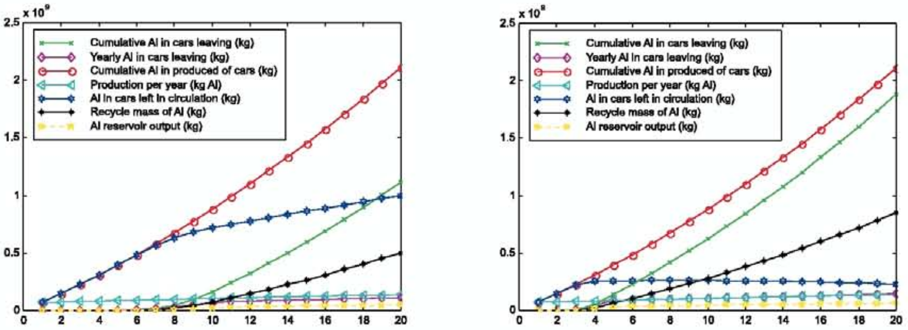
8.5.2 Optimization of the recycling of the car - various simulation results

The recycling optimization model calculates the recovery of the different elements dependent on the objective of the optimization. The examples below will present the results of the recycling optimization model in particular for the optimization of the recycling of aluminium in the car. As a result the model will give the recovery of aluminium (wrought and cast), steel, copper and the rest fraction (parameters b and c in Figure 8.2) for different kind of inputs as supplied by the dynamic model (whereas the input is dependent on changing lifetime, weight and composition of the car). These examples illustrate the influence of the various distribution functions as defined in the dynamic model on the recovery rate. The output $x(t)$ of the dynamic model for two different years of dismantling (see Table 8.1) is used as an input for the recycling optimization model.

The intermediate output of the dynamic model (Table 8.1) defines the composition and weight of the car at a certain moment in time (Year of Dismantling). The input for the recycling optimization model is only defined for one size class p, because all elements are assumed to be present as one size class -the car-, which is the largest size class defined in the

Table 8.1: Output dynamic model $x(t)$ for t_2=1 and t_2=10, for $f(t_1,t_2)$ (α=5 and β=15), $g(t_1,w)$ (α=7 and β=8),χ=1, τ=0, CR=0.9

Dismantling year Element $'k'$	t_2=1 [kg]	t_2=10 [kg]
Al wrought	24.10	33.37
Al cast	65.21	69.85
Steel	830.90	807.74
Copper	27.08	29.68
Remainder	311.21	317.69
Total	1258.50	1258.33



(a) (b)

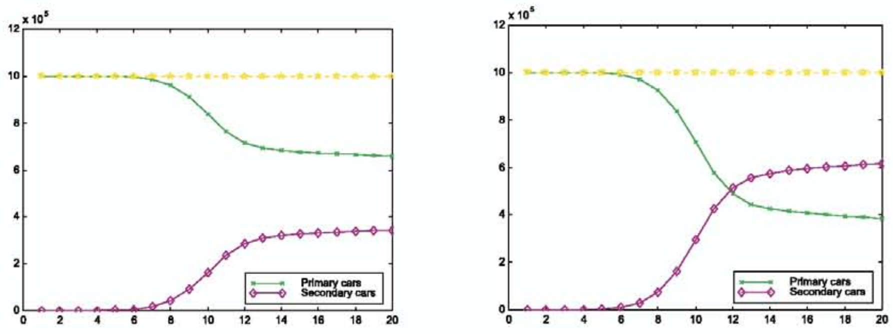
Figure 8.7: Number of cars and associated aluminium in circulation for a constant production rate of $\dot{C}$ =1,000,000, $f(t_1,t_2)$ ((a) α=8/β=10 and (b)α=13/β =5), $g(t_1,w)$ (α=7 and β=8), χ=1, τ=0, CR=0.9, RR=0.5 and t_2=1982

model. In this example, the weight of the car is kept constant over time, which is obviously not the case in practice [297]. As mentioned above, the changing weight of the car can easily be incorporated into the model.

Simplified flowsheet for optimization

A simplified flowsheet (Figure 8.9) has been derived from the detailed recycling flowsheet for ELV's (Figure 8.4)). This flowsheet (Figure 8.9), being the basis for the recycling optimization model for aluminium recycling as discussed here, gives the material flows and structure of aluminium recycling in ELV's.

The optimization is being performed for the dismantling, shredding and mechanical separation of the car as well as the metallurgical production of aluminium from the car as depicted in the flow sheet of Figure 8.9. The various unit operations included in the separation of the non-ferrous streams, like heavy medium separation, eddy current separation, image processing etc. are simplified by defining black boxes for two different scenarios for non-ferrous separation. The separation efficiencies of the different steps in these scenarios are combined into one linear equation for each scenario describing the total efficiency over the sequence of operations within these black boxes. In spite of this simplification the inseparable relationship



(a) (b)

Figure 8.8: of cars applying primary or secondary aluminium of the total production rate of $\dot{C}$ =1,000,000, for $f(t_1, t_2)$ (α=8/β=10), $g(t_1, w)$ α=7 and β =8), χ=1, τ=0, CR=0.9, RR=0.5 and t_2=1981 ($t_1 = 1$)

between mechanical recycling and metallurgical processing can be clearly illustrated. A more extended optimization can be performed describing each of the unit operations in the recycling flow sheet within non-ferrous separation. In order to describe the simplified optimization aluminium recycling, five different materials $'k'$ have been defined: Al-wrought, Al-cast, steel, copper and rest - containing all other elements, metals, and compounds of the car, except Al, steel and copper. Steel is included in the optimization of aluminium since it comprises the largest material stream in the car. Besides steel is a major contaminant in the recycling of aluminium. Copper is included being one of the most crucial impurities in steel recycling and playing an important role in the recycling of aluminium as well. For each element $'k'$ mass balance and separation constraints as given in equations Eq. 8.5 to Eq. 8.14 are defined around each unit operation included in the optimization sequence. The equations for separation efficiency are partly derived from experimental and industrial data [295, 330, 331, 332] providing recovery values or recovery-grade curves together with the range within which the linear equations are appropriate. It is surprising how poorly data often have been measured, due to the poor understanding of recycling systems and the lack of fundamental recycling theory. Since a lot of data on the performance of the various unit operations is very incomplete or very often even lacking, estimations for the process efficiencies had to be made to define the separation efficiency equations. The separation efficiency equations are derived based on data available or estimated for each unit operation individually. This could lead to some imperfections in the model over the whole sequence of unit operations in the recycling optimization flow sheet. However, this affects neither the usability of the system approach used to describe and optimise recycling systems nor the validity and applicability of the developed model as discussed above. It however emphasises the importance of proper data collection on a sound technological basis.

For the optimization of aluminium recycling in ELV's, as discussed here, more than 400 variables with regard to the different material streams are defined. Furthermore, 9 variables describing the structural parameters α_{ij} are added (values α_1, α_2, α_3, β_1, β_2, γ_1, γ_2, δ_1, δ_2 in Figure 8.9) in order to optimise the structure of the network.

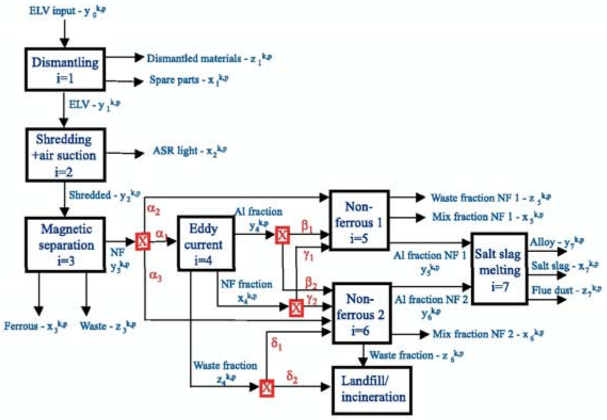


Figure 8.9: Simplified flow sheet for recycling aluminium in ELV's (with k = Al-wrought, Al-cast, steel, copper, remainder and $p = 1$ to 5)

Results of optimization

The objective for the optimization as performed in this example is the recovery of aluminium, which will be maximised in the optimization procedure. The results of the optimization for the two different input ranges (t_2=1 and t_2=10, see Table 8.1) are given in Table 8.2, Table 8.3, Table 8.4, Table 8.5, Table 8.6, Table 8.7, Table 8.8, and Table 8.9 showing the optimised material streams (Table 8.2) and (Table 8.3), grades (Table 8.4) and (Table 8.5), recoveries (Table 8.6) and (Table 8.7) for Al-wrought and Al-cast, the alloy composition of the output stream of the metallurgical production of aluminium (Table 8.8) and the structural parameters (Table 8.9) within this optimised flow sheet. Since the optimization focuses on aluminium, only the results for this material stream (wrought and cast aluminium) are presented below. Similar simulation results are created by the model for the other elements (steel, copper, and remainder).

Although the model generates the grade and recovery values for each of the size classes p for all different material streams, only the total grade and recovery of the various material flows are represented in Table 8.4 to Table 8.7.

Recovery rate

The total recovery rate for the different elements as calculated by the recycling optimization model is represented in Table 8.10 (given the defined objective function and restricted by the various constraints on recovery and grade of the various unit operations and the required output quality of the produced aluminium alloy). The recovery rate for the various elements is composed out of the recovery for all unit operations included in the optimization (see Table 8.6 and Table 8.7). The objective of the optimization is to maximise the total output of aluminium (sum of wrought and cast). The model will calculate an optimal solution for this objective, which means that not always both recoveries will be optimised under given constraints on the model, but the most optimal solution for the defined objective will be derived (this includes the optimization of the structure of the network as well, as depicted in Table 8.9). This explains the decreasing recovery of Al-wrought for the year t_2. Since the optimization is focused on the recovery of aluminium, no process routes for recycling of the remainder are defined in the recycling optimization model yet. As a consequence the recovery rate for this fraction is assumed to be zero, which is obviously not representing reality.

Table 8.10 illustrates the influence of the changing lifetime, weight and composition of the car as expressed by the various distribution functions in the dynamic model on the recovery rate of the different elements present in the car. The recycling optimization model provides input values for the recovery rate (RR^k) for the different elements k for the dynamic model. Figure 8.8 illustrated the effect of the changing recovery rate on the response to the recycling system. Similar simulations as are discussed above for aluminium can be performed for any other element being recycled from the car.

8.6 Discussion

Due to the time-varying weight, composition and complexity of multi-component products such as cars, recycling is complicated. The recovery rate of the materials present in the car and hence the recycling rate of the car is determined by the dynamics of the resource cycle, determining the input of the recycling system as well as by the performance of the recycling system, which involves a network of interconnected processes and material and energy flows.

Table 8.2: Results of optimization - Optimised material streams Al-wrought [kg]

Description of material stream	Size class p	Variable	optimization results year $t_2 = 1$	optimization results year $t_2 = 10$
Al wrought in ELV	size class 1	y111	17.99	20.07
Al wrought in spare parts	size class 1	x111	6.12	13.29
Al wrought in dismantled materials	size class 1	z111	0.00	0.00
Al wrought in shredded	size class 1	y211	2.17	2.32
Al wrought in shredded	size class 2	y212	3.27	3.47
Al wrought in shredded	size class 3	y213	3.23	3.39
Al wrought in shredded	size class 4	y214	1.04	1.16
Al wrought in shredded	size class 5	y215	1.08	1.16
Al wrought in ASR light	size class 1	x211	1.44	1.69
Al wrought in ASR light	size class 2	x212	2.14	2.55
Al wrought in ASR light	size class 3	x213	2.16	2.62
Al wrought in ASR light	size class 4	x214	0.75	0.84
Al wrought in ASR light	size class 5	x215	0.71	0.84
Al wrought in NF	size class 1	y311	1.89	2.09
Al wrought in NF	size class 2	y312	2.71	3.01
Al wrought in NF	size class 3	y313	2.80	3.02
Al wrought in NF	size class 4	y314	0.92	1.06
Al wrought in NF	size class 5	y315	0.90	1.10
Al wrought in ferrous	size class 1	x311	0.29	0.14
Al wrought in ferrous	size class 2	x312	0.02	0.02
Al wrought in ferrous	size class 3	x313	0.01	0.02
Al wrought in ferrous	size class 4	x314	0.02	0.00
Al wrought in ferrous	size class 5	x315	0.02	0.00
Al wrought in waste	size class 1	z311	0.00	0.07
Al wrought in waste	size class 2	z312	0.55	0.43
Al wrought in waste	size class 3	z313	0.43	0.31
Al wrought in waste	size class 4	z314	0.11	0.11
Al wrought in waste	size class 5	z315	0.17	0.05
Al wrought in Al fraction EC	size class 1	y411	1.79	1.99
Al wrought in Al fraction EC	size class 2	y412	0.96	0.99
Al wrought in Al fraction EC	size class 3	y413	2.61	2.96
Al wrought in Al fraction EC	size class 4	y414	0.91	0.98
Al wrought in Al fraction EC	size class 5	y415	0.76	1.08
Al wrought in NF fraction EC	size class 1	x411	0.09	0.11
Al wrought in NF fraction EC	size class 2	x412	0.10	0.54
Al wrought in NF fraction EC	size class 3	x413	0.00	0.03
Al wrought in NF fraction EC	size class 4	x414	0.01	0.01
Al wrought in NF fraction EC	size class 5	x415	0.10	0.01
Al wrought in waste fraction EC	size class 1	z411	0.00	0.00
Al wrought in waste fraction EC	size class 2	z412	1.63	1.49
Al wrought in waste fraction EC	size class 3	z413	0.18	0.03
Al wrought in waste fraction EC	size class 4	z414	0.00	0.07
Al wrought in waste fraction EC	size class 5	z415	0.04	0.01
Al wrought in Al fraction NF 1	size class 1	y511	1.49	1.15
Al wrought in Al fraction NF 1	size class 2	y512	0.70	0.57
Al wrought in Al fraction NF 1	size class 3	y513	2.02	1.72
Al wrought in Al fraction NF 1	size class 4	y514	0.76	0.60
Al wrought in Al fraction NF 1	size class 5	y515	0.64	0.67
Al wrought in mix fraction NF 1	size class 1	x511	0.00	0.00
Al wrought in mix fraction NF 1	size class 2	x512	0.00	0.03
Al wrought in mix fraction NF 1	size class 3	x513	0.05	0.01
Al wrought in mix fraction NF 1	size class 4	x514	0.00	0.00
Al wrought in mix fraction NF 1	size class 5	x515	0.00	0.00
Al wrought in waste fraction NF 1	size class 1	z511	0.00	0.06
Al wrought in waste fraction NF 1	size class 2	z512	0.08	0.03
Al wrought in waste fraction NF 1	size class 3	z513	0.08	0.10
Al wrought in waste fraction NF 1	size class 4	z514	0.00	0.01
Al wrought in waste fraction NF 1	size class 5	z515	0.00	0.00
Al wrought in Al fraction NF 2	size class 1	y611	0.42	0.88
Al wrought in Al fraction NF 2	size class 2	y612	1.92	2.41
Al wrought in Al fraction NF 2	size class 3	y613	0.65	1.17
Al wrought in Al fraction NF 2	size class 4	y614	0.18	0.45
Al wrought in Al fraction NF 2	size class 5	y615	0.27	0.43
Al wrought in mix fraction NF 2	size class 1	x611	0.00	0.00
Al wrought in mix fraction NF 2	size class 2	x612	0.01	0.00
Al wrought in mix fraction NF 2	size class 3	x613	0.01	0.02
Al wrought in mix fraction NF 2	size class 4	x614	0.00	0.01
Al wrought in mix fraction NF 2	size class 5	x615	0.01	0.02
Al wrought in waste fraction NF 2	size class 1	z611	0.00	0.00
Al wrought in waste fraction NF 2	size class 2	z612	0.00	0.00
Al wrought in waste fraction NF 2	size class 3	z613	0.00	0.01
Al wrought in waste fraction NF 2	size class 4	z614	0.00	0.01
Al wrought in waste fraction NF 2	size class 5	z615	0.00	0.00
Al wrought in alloy	size class 1	y711	8.38	9.46
Al wrought in salt flux	size class 1	x711	0.24	0.28
Al wrought in fine dusts	size class 1	z711	0.68	0.75

Table 8.3: Results of optimization - Optimised material streams cast-wrought [kg]

Description of material stream	Size class p	Variable	optimization results year $t_2 = 1$	optimization results year $t_2 = 10$
Al cast in ELV	size class 1	y121	39.12	41.92
Al cast in spare parts	size class 1	x121	26.08	16.34
Al cast in dismantled materials	size class 1	z121	0.00	11.58
Al cast in shredded	size class 1	y221	6.89	7.32
Al cast in shredded	size class 2	y222	10.36	10.94
Al cast in shredded	size class 3	y223	10.31	10.94
Al cast in shredded	size class 4	y224	3.38	3.66
Al cast in shredded	size class 5	y225	3.44	3.66
Al cast in ASR light	size class 1	x221	0.92	1.08
Al cast in ASR light	size class 2	x222	1.37	1.62
Al cast in ASR light	size class 3	x223	1.41	1.64
Al cast in ASR light	size class 4	x224	0.52	0.54
Al cast in ASR light	size class 5	x225	0.46	0.54
Al cast in NF	size class 1	y321	6.32	7.07
Al cast in NF	size class 2	y322	9.26	10.28
Al cast in NF	size class 3	y323	9.49	10.42
Al cast in NF	size class 4	y324	3.13	3.52
Al cast in NF	size class 5	y325	3.05	3.63
Al cast in ferrous	size class 1	x321	0.47	0.26
Al cast in ferrous	size class 2	x322	0.29	0.13
Al cast in ferrous	size class 3	x323	0.54	0.51
Al cast in ferrous	size class 4	x324	0.00	0.00
Al cast in ferrous	size class 5	x325	0.37	0.00
Al cast in waste	size class 1	z321	0.09	0.00
Al cast in waste	size class 2	z322	0.79	0.53
Al cast in waste	size class 3	z323	0.27	0.00
Al cast in waste	size class 4	z324	0.26	0.13
Al cast in waste	size class 5	z325	0.01	0.02
Al cast in Al fraction EC	size class 1	y421	5.96	6.67
Al cast in Al fraction EC	size class 2	y422	3.13	3.11
Al cast in Al fraction EC	size class 3	y423	8.86	9.98
Al cast in Al fraction EC	size class 4	y424	3.08	3.24
Al cast in Al fraction EC	size class 5	y425	2.53	3.61
Al cast in NF fraction EC	size class 1	x421	0.02	0.03
Al cast in NF fraction EC	size class 2	x422	0.00	0.06
Al cast in NF fraction EC	size class 3	x423	0.50	0.42
Al cast in NF fraction EC	size class 4	x424	0.04	0.27
Al cast in NF fraction EC	size class 5	x425	0.40	0.01
Al cast in waste fraction EC	size class 1	z421	0.29	0.38
Al cast in waste fraction EC	size class 2	z422	6.05	7.10
Al cast in waste fraction EC	size class 3	z423	0.05	0.01
Al cast in waste fraction EC	size class 4	z424	0.00	0.00
Al cast in waste fraction EC	size class 5	z425	0.08	0.00
Al cast in Al fraction NF 1	size class 1	y521	4.92	3.81
Al cast in Al fraction NF 2	size class 2	y522	2.33	1.86
Al cast in Al fraction NF 3	size class 3	y523	6.71	5.68
Al cast in Al fraction NF 4	size class 4	y524	2.52	1.99
Al cast in Al fraction NF 5	size class 5	y525	2.11	2.23
Al cast in mix fraction NF 1	size class 1	x521	0.00	0.00
Al cast in mix fraction NF 1	size class 2	x522	0.00	0.05
Al cast in mix fraction NF 1	size class 3	x523	0.00	0.00
Al cast in mix fraction NF 1	size class 4	x524	0.00	0.00
Al cast in mix fraction NF 1	size class 5	x525	0.00	0.00
Al cast in waste fraction NF 1	size class 1	z521	0.03	0.30
Al cast in waste fraction NF 1	size class 2	z522	0.27	0.00
Al cast in waste fraction NF 1	size class 3	z523	0.65	0.46
Al cast in waste fraction NF 1	size class 4	z524	0.02	0.00
Al cast in waste fraction NF 1	size class 5	z525	0.00	0.00
Al cast in Al fraction NF 2	size class 1	y621	1.30	2.94
Al cast in Al fraction NF 2	size class 2	y622	6.49	8.17
Al cast in Al fraction NF 2	size class 3	y623	2.11	4.04
Al cast in Al fraction NF 2	size class 4	y624	0.57	1.48
Al cast in Al fraction NF 2	size class 5	y625	0.87	1.38
Al cast in mix fraction NF 2	size class 1	x621	0.00	0.02
Al cast in mix fraction NF 2	size class 2	x622	0.14	0.00
Al cast in mix fraction NF 2	size class 3	x623	0.00	0.00
Al cast in mix fraction NF 2	size class 4	x624	0.00	0.00
Al cast in mix fraction NF 2	size class 5	x625	0.01	0.00
Al cast in waste fraction NF 2	size class 1	z621	0.01	0.00
Al cast in waste fraction NF 2	size class 2	z622	0.02	0.18
Al cast in waste fraction NF 2	size class 3	z623	0.01	0.20
Al cast in waste fraction NF 2	size class 4	z624	0.01	0.02
Al cast in waste fraction NF 2	size class 5	z625	0.05	0.01
Al cast in alloy		y72	27.82	31.58
Al cast in salt flux		x72	0.85	0.97
Al cast in flue dusts		z72	0.00	0.21

Table 8.4: Results of optimization - grade after optimization Al-wrought [-]

Grade	optimization results year $t_2 = 1$	optimization results year $t_2 = 10$
Gy11	0.01	0.02
Gx11	0.13	0.45
Gy21	0.01	0.01
Gy31	0.07	0.06
Gx31	0.00	0.00
Gy41	0.10	0.09
Gx41	0.01	0.01
Gx51	0.12	0.03
Gy51	0.23	0.23
Gy61	0.22	0.22
Gx61	0.04	0.01

Table 8.5: Results of optimization - recovery after optimization Al-cast [-]

Recovery	optimization results year $t_2 = 1$	optimization results year $t_2 = 10$
Gy12	0.03	0.03
Gx12	0.54	0.55
Gy22	0.03	0.03
Gy32	0.23	0.20
Gx32	0.00	0.00
Gy42	0.33	0.31
Gx42	0.02	0.01
Gx52	0.02	0.03
Gy52	0.76	0.76
Gy62	0.73	0.74
Gx62	0.15	0.01

Table 8.6: Results of optimization - recovery after optimization Al-wrought [-]

Recovery	optimization results year $t_2 = 1$	optimization results year $t_2 = 10$
Ry11	0.75	0.60
Rx11	0.25	0.40
Ry21	0.60	0.57
Ry31	0.85	0.90
Rx31	0.03	0.02
Ry41	0.77	0.78
Rx41	0.03	0.07
Rx51	0.01	0.01
Ry51	0.96	0.95
Ry61	0.99	0.99
Rx61	0.01	0.01
Ry71	0.90	0.90
Rx71	0.03	0.03

Table 8.7: Results of optimization - recovery after optimization Al-cast [-]

Recovery	optimization results year $t_2 - 1$	optimization results year $t_2 - 10$
Ry12	0.60	0.60
Rx12	0.40	0.23
Ry22	0.88	0.87
Ry32	0.91	0.96
Rx32	0.05	0.02
Ry42	0.76	0.76
Rx42	0.03	0.02
Rx52	0.00	0.00
Ry52	0.95	0.95
Ry62	0.98	0.98
Rx62	0.01	0.00
Ry72	0.97	0.96
Rx72	0.03	0.03

Table 8.8: Results of optimization - Alloy composition of output [-]

Element in alloy	optimization results year $t_2 = 1$	optimization results year $t_2 = 10$
Al	0.86	0.85
Si	0.10	0.09
Fe	0.01	0.01
Cu	0.02	0.02
Mg	0.02	0.02
Others	0.00	0.00

Table 8.9: Results of optimization - Optimised structural parameters

Structural parameter	optimization results year $t_2 = 1$	optimization results year $t_2 = 10$
1	0.99	1.00
2	0.00	0.00
3	0.01	0.00
1	0.83	0.62
2	0.17	0.38
1	0.00	0.02
2	1.00	0.98
1	1.00	1.00
2	0.00	0.00

Table 8.10: Output of recycling optimization model, RR, for different elements for $t_2 = 1$ and $t_2 = 10$, for $f(t_1, t_2)$ (α=5 and β=15), $g(t_1, w)$ (α=7 and β=8), χ=1, τ=0, CR=0.9

Dismantling year Element $'k'$	t_2=1 RR [-]	t_2=10 RR [-]
Al wrought	0.35	0.28
Al cast	0.43	0.45
Steel	0.99	0.99
Copper	0.43	0.12
Remainder	0	0

- Improving the efficiency of the material cycle of the car to comply with the recycling targets imposed by EU legislation, whereas economy is the driving force, requires insight into all aspects influencing the closing of the material cycle (dynamics, technology, design, economy, legislation, etc.) and their mutual relation. This is only possible if recycling systems are described more fundamentally than has been the case up till now, which requires solid technological knowledge on the behaviour of processes and materials within the recycling system as well as the understanding of the dynamics of the system.

- Closing of the material cycle requires a resource cycle system approach (Resource cycle, see Figure 8.1), in which the mutual compatibility of the successive processes of mechanical recycling and metallurgical operations within this interconnected resource cycle system are made transparent and are optimised (Technology cycle, see Figure 8.1). Of critical importance in this are the material quality, type and shape at various stages in the recycling chain, which are strongly determined by product design (mineralogy) and technological state-of-the art.

- The varying complex composition of cars with time, as well as the varying lifetimes of the product (which are partly determined by the product design) determine the input of the recycling system and therefore affect the recovery and recycling rate to be achieved. In addition, economy and restrictions on environmental impact also affect the closing of the resource cycle.

- A dynamic model has been developed which analyses and optimises these time dependent complex interactions. The dynamic model describing the behaviour of the system over time, in combination with the fundamental modelling and optimization of the recycling system, is required to determine the influence of the changing lifetime, weight and composition of the car on the recovery rate and the inventory of the system. Therefore knowledge on the effect of material characteristics and quality of intermediate recycling streams on the recovery rate has to be integrated part of this resource cycle system approach.

- The effect of the changing recovery rate on the response to the system and the ratio between primary and secondary (metallurgical) production becomes clear from simulations using the dynamic and recycling optimization model, and is largely influenced by the time delay of the system.

- Fundamental theory on process engineering and minerals processing technology has been used to model the complex recycling system of the car. The more precise definition of recovery rate and the recycling system in the manner presented here, together with the dynamic and recycling optimization model provides an improved and more fundamental basis for describing and optimising these complex resource cycle systems. This has been lacking up till now.

- The developed models can assist in applying design for recycling, improving recycling legislation but also provide valuable metal inventory and economic insights into the various interconnected metal cycles within the resource cycle system of products.

8.7 Examples and case study

8.7.1 Monitoring and chain management for ELV recycling

In view of the recycling/recovery targets of 85% (2006) and 95% (2015) to be achieved for end-of-life vehicle recycling according to the EU directive (Directive 2000/53/EC), the questions should be asked: "How can the recycling of ELV's be monitored in an objective way, in order to investigate and communicate the feasibility of the EU directive on ELV's and calculate the recycling rate".

Answer

Fundamental theory is required as a common language to investigate and communicate the feasibility and realisation of the ELV recycling targets as laid down by the EU directive (Directive 2000/53/EC) as well as to calculate and proof the achieved recycling rate on industrial recycling plants. Based on fundamental recycling theory developed by the authors, on the experience among others of a large scale industrial recycling experiment and applying classical sampling theory and data reconciliation, it has been shown in this chapter that:

- The recycling rate and EU targets should always be presented with its standard deviation or error margin. The recycling rate and its error margin or standard deviation are determined by the statistics of the mass balance for each of the elements present in the car and the distributed properties such as life-time .
- Control and prediction of the quality of recycling (intermediate) streams is essential to ensure that the feed to metallurgical processing permits the economic production of quality metal products, with minimal losses and emissions.
- A chain management approach for monitoring is required; all players in the recycling chain must obey to the procedure of proper sampling and data collection for the calculation of the recycling rate, based on a closed mass balance, all within a statistical framework. Monitoring of the recycling rate calculations should take into consideration the integrity and control of the data over the whole recycling chain (dismantling, shredding, physical separation processes, metallurgy, and thermal treatment) for the different materials present in the car.

A common language for the monitoring and determination of the recycling rate can only be established if fundamental theoretical models (Figure 8.10) are used and adopted by the industry and EU in order to calculate statistically and fundamentally reliable recycling rates. These fundamental recycling models take into consideration (i) material quality; (ii) separation physics and thermodynamics; (iii) losses and emissions; (iv) plant/flowsheet architecture; (v) distributed and dynamic properties, of present and future car designs. This permits:

- Monitoring
- Assessment of present recycling plants/recycling schemes
- Evaluation of different recycling routes
- Evaluation of the feasibility of the recycling targets of the EU
- Identification of requirements for future recycling technology development for future light weight car designs

Environmental recycling scores and economic evaluation Any evaluation of the economic and/or environmental consequences and calculation of environmental scores of ELV recycling can only be carried out based on the monitoring procedure and fundamental recycling models as discussed above. Only then an objective, reliable and industrial relevant answer can be generated, in which material quality and recovery rates for the different processes (controlled by physics and thermodynamics) per material/compound are addressed within a statistical and dynamic (time-dependant) framework. LCA is not enough!

Summary Chain management and monitoring is required over the total recycling system, based on fundamental metrics such as discussed above. Without this fundamental basis it can be questioned to what extent the different actors within the recycling chain can be held responsible for their performance. High environmental standards and recycling rates can only be achieved and maintained through proper understanding of the complex interactions in the recycling system, in which the distributed properties of product design, high efficiency and competence of physical separation plants, material quality and economics in relation to metallurgical and thermal processing play a crucial role in achieving high recycling rates.

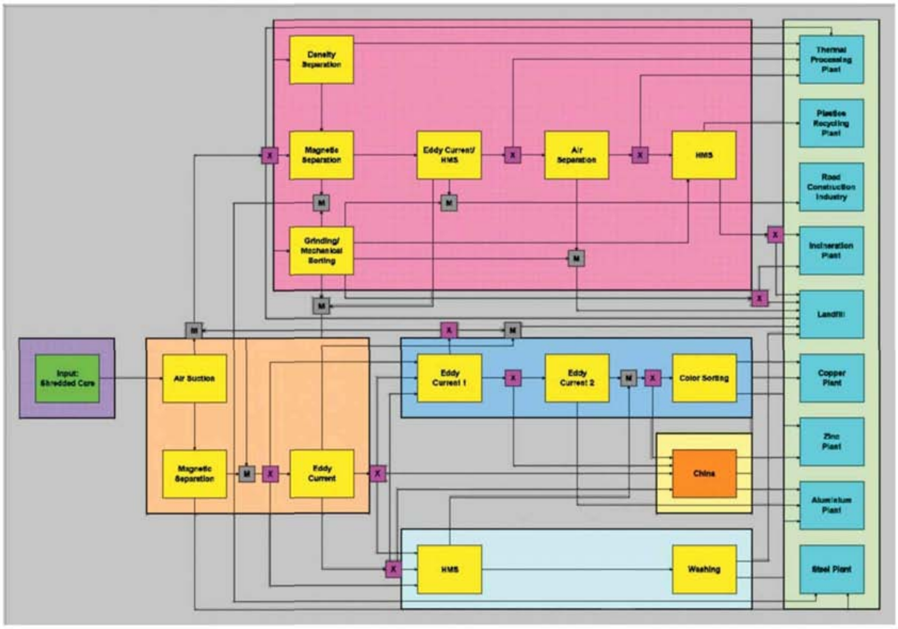


Figure 8.10: Flow sheet of recycling (optimization) model including processes (physical, metallurgical and thermal treatment), process efficiencies and material flows and quality of recycling (intermediate) products

Nomenclature

a_p, b_p	Parameters in grade-recovery relationships for a particle size class p
α_{ij}	Structural parameters linking unit operation j with i
$\dot{C}$	Production rate of cars (cars/year)
CR	Collection rate
$Cf_i^{k,p}$	Organic content of metal fraction for element k in particle size class p
$f(t, \alpha, \beta)$	Weibull distribution function with parameters α and β
$f(t_1, t_2)$	Distribution function as a function of Years of production and dismantling
$f_i^{k,p}$	Feed of element k in particle size class p for unit operation i (kg)
$g(t_1, w)$	Weight distribution
$Gy_i^{k,p}$	Grade of element k in particle size class p in stream y for unit operation i
$h^k(w, mp^k, t_l)$	Mass percentage distribution as a function of weight class w, mass percentage mp and years of production for each element i
mp^k	Mass percentage class of element k
i, j	plants, unit operations, transport, etc., with $1 \rightarrow n$ representing the total amount of units (dismantling, shredding, magnetic separation, non-ferrous separation, metallurgical unit operations, etc.)
k	elements, metals, compounds originating from the different material streams in the recycling flow sheet of end-of-life vehicles (Al wrought, Al cast, steel, copper, other materials such as other non-ferrous metals, organic materials, glass, etc.)
$m^k(t)$	Production of product for element k (number or kg)
p	Particle size class p
$p^k(t)$	Primary product for element k (number or kg)
Sf_i^{k,p_j,p_y}	Transformation matrix of particle size reduction during shredding
RR^k	Recovery rate of element k
$Ry_i^{k,p}$	Recovery of element k in particle size class p to stream y for unit operation i
$s^k(t)$	Secondary material after recycling after stockpile for element k (number or kg)
t, t_1, t_2	Year, Year of production and Year of dismantling respectively
w	Weight class
$x^k(t)$	End-of-life product for element k (number or kg)
$x_i^{k,p}$	Flow rate of element k in particle size class p in stream x of unit operation i (kg)
$y_1 - y_4$	Cumulated mass
$y_i^{k,p}$	Flow rate of element k in particle size class p in stream y for unit operation i (kg)
YD	Year of dismantling
YP	Year of production
$z^k(t)$	Secondary material produced after separation plant for element k (number or kg)

χ	Flow parameter from reservoir
τ	Time delay (year)

Chapter 9

The role of particle size reduction, liberation and product design in recycling passenger vehicles

The quality of recycling intermediate products created during shredding and physical separation is of critical importance to ensure that the feed to metal producing processes permits the economic production of quality metal products. The liberation of materials during shredding plays an important role in the composition and quality of the intermediate recycling streams. The degree of liberation of the materials present in the car as well as the particle size reduction during shredding are of major influence on the separation efficiency of physical separation processes. Moreover it affects the purity of the material streams produced by separation and thus the metallurgical process efficiency, and hence the ultimate material recovery and therefore the recycling rate. Therefore, it is essential to capture the particle size and degree of liberation in the recycling models, which provide a fundamental framework for the optimization of the recycling rate as well as for the calculation and prediction of the recycling rate. Since particle size reduction and liberation are closely related to the design of the product (material combinations and connections) it should be included in the models in order to link design to recycling. Two different models are developed to describe the influence of liberation and particle size reduction on the recycling (rate) of end-of-life vehicles. These models have been developed based on the knowledge of traditional mineral processing. It is illustrated that the modelling of traditional minerals processing systems can be applied in the new field of (design for) recycling of complex consumer products. From the various simulations presented it can be concluded that the modelling of the breakage behaviour for modern consumer products differs fundamentally from traditional minerals processing. Moreover various theoretical simulations will illustrate the effect of changes in product design and hence particle size reduction and liberation on the recovery rate for the various materials in the car and therefore on the recycling rate of end-of-life vehicles. This chapter illustrates that the development of fundamental models is indispensable to build the bridge between the material combinations and connections in design and the recycling of cars in order to increase recycling rates as well as to provide a framework to link design to recycling. Liberation and particle size reduction during shredding is the link between design and recycling.

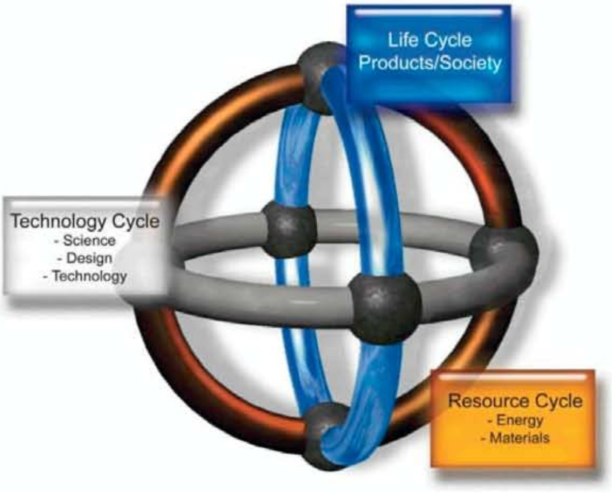


Figure 9.1: Modelling the role of particle size reduction, liberation and product design in recycling passenger vehicles - combining the Technology cycle and the Resource cycle

9.1 Introduction

In Chapter 8 the quality control of recycling intermediate products created during shredding and physical separation is discussed. This highlights the critical importance that the feed to metal producing processes has on the (economic) production of quality metal products [51] subject to the high recycling targets imposed by EU legislation. The developed models describe the optimization of the recovery and recycling of the materials in the car not only as a function of the dynamics of the design of the car and the efficiency of the separation processes, but also as a function of the material characteristics and therefore of the quality of the recycling (intermediate) products. However in order to be able to apply design for recycling, a closer link is required between the materials combinations and connections in the design and the separation efficiency and quality of recycling (intermediate) products as described by the discussed models. This aspect will be discussed in this chapter. It is known from traditional minerals processing technology that the behaviour of ore dressing equipment depends on the nature of the individual particles processed [333, 334]. King [334] and Heiskanen [333] discuss that the two most important fundamental properties are the size of the particle and its mineralogical composition, which are both determined by the comminution process. Mineral liberation is the natural link between comminution and mineral recovery operations. Modelling of mineral separation therefore requires the modelling of liberation phenomenon. Therefore, it can be concluded that the same principle applies for the separation of 'artificial' ores, such as modern consumer products, of which the mineralogy is determined by design. The design of modern products, such as the car, combines and connects various materials in many complex different ways, making up the complex 'mineralogy' of the car and its components [51]. This 'mineralogy' changes rapidly and continuously over time and is directly related to the liberation and composition of the intermediate recycling products after physical separation.

On the other hand, the mineralogy of traditional primary ores and minerals originating from mines, from which the composition is well known, does not change drastically from a particular mine site or even between mine sites. The simulation of classical minerals processing is often not easy due to incomplete descriptions of mineral properties, making the calibration of fundamental models difficult. Modern society 'minerals' are complex, so diverse and changing so rapidly making a fundamental description extremely difficult. It can be stated that liberation during shredding is the link between design and recycling operations. Particle size reduction and liberation of materials during the shredding of modern end-of-life products are closely related to the design of the product (Technology cycle, see Figure 9.1) and play an important role in the composition and quality of the intermediate recycling streams and the ultimate material recovery and therefore the recycling rate (Resource cycle, see Figure 9.1). In this chapter the development of two different recycling optimization models will be discussed, in addition to the recycling optimization model developed in Chapter 8, describing the relationship between product design ('mineralogy'), mechanical separation efficiency and metallurgy as a function of:

- liberation during shredding, and;
- the combination of particle size reduction and liberation during shredding;

which will affect the recycling rate of cars.

The three different recycling optimization models as discussed in respectively Chapters 8 and Chapter 9 each focus on a different aspect of the intersections between the three cycles (see Figure 9.1), which all affect the recycling rate and optimization of end-of-life vehicles. The main focus of each of the recycling optimization models is briefly described below. The first recycling optimization model as discussed in Chapter 8 describes the recycling system and the calculation of the recycling rate of the car as a function of the performance of the various unit operations on the basis of their individual grade/recovery relationship. The calculations and optimization of the recycling system are placed within the dynamic framework of the resource cycle of the car as described by the dynamic resource cycle model. The calculations are based on normal plant practice, in which the particle size of the material flows is affecting the material flows throughout the plant. The assumption is made that the different particles after shredding only consist of one component. The second recycling model as will be discussed in the first section of this chapter describes the relation between design (material combinations and connections) and liberation of the materials during shredding. The separation efficiency is modelled based on recovery factors, which are dependent on the degree of liberation of the materials.

The third model as will be described in the second part of this chapter calculates and optimises the recycling rate of end-of-life vehicles as a function of both particle size reduction and liberation during shredding. This model provides a first principles technological basis to develop the link between design and recycling. In this model the separation efficiency is described by recovery factors, which are a function of particle size class and the degree of liberation of the material flows. In the first model, the grade is implicitly part of the modelling parameters. In addition, the composition of each of the material flows within the recycling flowsheet can be calculated. For the second and third model, the grade and composition can be calculated from the model, not only based on the general composition of the material streams, but including the effect of the material combinations present in the non-liberated particles. The calculation and control of the grade is crucial for the recycling rate to be achieved, in view of the quality control of (intermediate) recycling products being the input for metallurgical processing. The second and third recycling optimization models, which will capture the role of liberation (and particle size reduction) will be developed partly based on the modelling techniques applied in traditional minerals processing demonstrating how classical theory can be applied to solve modern problems. The inseparable relationship between product design, product mineralogy, and liberation of materials in relation to mechanical separation technology and quality requirements for metallurgical material recovery processes will be captured by the two different system models for the optimization of the resource cycle of passenger vehicles. The development of first principles models is indispensable to build the bridge between the material combinations and connections in design and the recycling of cars. This will illustrate at the same time how the knowledge of traditional mineral processing can be applied in the new field of design for recycling of complex consumer products. On the longer term, this could become the future of minerals processing technology, since legislation and environmental concern will increase the availability of secondary materials, being the mineral ores of the future.

The inseparable link between product design (Technology cycle, see Figure 9.1), and the particle size reduction and liberation of materials in relation to mechanical separation technology and quality requirements for metallurgical material recovery processes and hence the recycling rate of the product (Resource cycle, see Figure 9.1) is captured by the models as described in this chapter. This chapter operates on the link between the Technology and the Resource cycle (Figure 9.1).

9.2 Recycling optimization model linking the liberation to the recycling rate of end-of-life vehicles

The liberation of materials during shredding plays an important role in the composition and quality of the intermediate recycling streams. The degree of liberation of the materials present in the car is of major influence on the separation efficiency of physical separation processes. Moreover it affects the purity of the material streams produced by physical separation and thus the metallurgical process efficiency. In general an increased complexity of recycling pyrometallurgy has arisen through the development and design of modern consumer products (such as passenger vehicles). Modern products contain a combination of metals that are not linked in the natural resource systems (Figure 1.2) [33]. As a consequence, these materials are not always compatible with the current processes in the metals production network, that was developed for the processing of primary natural resources and therefore, optimised for the processing of the primary metal and all mineralogically associated valuable and harmful minor elements. The formation of complex residue streams or undesired harmful emissions that cannot be handled in the current system inhibits thus the processing and recycling of those products at their end-of-life and will immediately result in decreasing recycling rates of these products. Losses within the recycling phase are e.g. caused by increasing product complexity and changing material combinations (see Figure 1.2), which affect liberation, efficiency of separation and the quality of intermediate recycling streams. Even a small change in product mineralogy (material combinations and connections) due to changing product design can have a significant effect on the final metal recovery and thus on the recycling rate of a product. The final metal recovery is dictated by the prevalent thermodynamics and kinetics of the metallurgical processes, which are the closers of the material cycle [33]. The strict limits to the presence of contaminations present in the input of metallurgical processes (e.g. $<0.25\%$ Cu in the ferrous scrap, $<0.3\%$ Fe in aluminium for certain alloy types, etc.) indicates that only a small amount of contaminant present in intermediate recycling streams, either due to imperfect liberation and/or separation in combination with a changed product design can lead to a decreased recovery and losses during the recycling of the product. Product designers, physical liberation and separation plants, waste processors, metal producers and decision makers must cooperate to obtain an optimal material and metal recovery in processing discarded consumer products. High environmental standards and recovery rates can only be achieved and maintained through proper understanding of these complex interactions, which are strongly dominated by continuously changing product design.

The assumption has been made in the model as discussed in Chapter 8 that the particles consist of only one material, and are completely liberated during shredding, which is not necessarily the case for all particles. Shredding will not liberate all combined materials. In order to include the influence of product design (mineralogy), liberation, and particle composition in the description and optimization of recycling systems, the model as discussed in Chapter 8 [51] therefore has to be expanded with a liberation model. This recycling optimization model predicts the recovery rate for the various materials present in the car as a function of product design and liberation in relation to the efficiency of the different physical and metallurgical process steps and the quality of the intermediate recycling streams due to imperfect liberation and separation. Product design and liberation will have a direct influence on the realisation of the targets laid down by legislation. The importance of including the degree of liberation in the model and its role in the material quality of the intermediate recycling streams is illustrated throughout the model and the case studies presented.

9.2.1 Phase description of the material streams

In order to capture the influence of material combinations determined by design and the degree of liberation (and thus the material combinations in the non-liberated particles) on the recovery rate and recycling of products, the model must be able to describe the first principles of the liberation of the different materials as a consequence of material combinations and joint types chosen during design and as a consequence of shredding. The degree of liberation will be determined by the performance and operation of the shredder, as well as by the material combinations and connections in the car. The developed liberation model describes the degree of liberation of a product (defined as a mineral, which is derived from classical minerals processing) by defining the fraction of the various materials present in the particles for a range of liberation classes. Table 9.1 summarises an example for the definition of the composition of the liberation classes in the model for a mineral A (in this case a mineral with Al-wrought being the major component). Similarly minerals B (Al-cast rich), C (Plastic rich/rest), D (Steel-rich) and E (Cu-rich) are being defined for the example of a five component recycling system. The material combinations in the as given in Table 9.1(c) are a direct consequence of the material combinations defined during design. The material flows in the recycling flowsheet are described based on the various minerals, of which the composition is given over the defined liberation classes based on the elements/materials included in the model. For each of the defined minerals, a similar matrix has been developed. Since data on the composition of the various liberation classes have never been measured up till now, estimations on this had to be made as can be seen from Table 9.1. The transformation of the liberation classes due to the shredding operation is defined in the model based on a transformation matrix. This is similar as defined by Reuter and Van Deventer [309] for milling and flotation plants. The output of the metallurgical processes has to comply with constraints on the alloy composition. Since each element is described separately in the liberation matrices (see Table 9.1) composing the various minerals, the output of the metallurgical operation can be calculated by adding the different materials present in one stream (e.g. the produced aluminium alloy). Aluminium is described in the model as wrought or cast, each with its own specific (average) composition, which is described in a matrix in the model. Together with the contaminants or alloying elements ending up in the alloy, the exact alloy composition can be calculated from the model based on the degree of liberation and can be controlled by defining boundary conditions on the output. Primary materials (aluminium and alloying elements) often have to be added to produce a required alloy composition. Input of primary materials must be kept to a minimum, for economical and environmental reasons. This can be realised by including the primary materials in the objective function for optimization.

9.2.2 Formulation of the recycling optimization model

The major difference between the recycling optimization model as described in Chapter 8 and the liberation model discussed here, is that the material streams are not defined based on elements k and particle size classes p, but in terms of minerals m, ranging from A to E and liberation classes l from 1 to 5 (Table 9.1). The liberation model describes the flow of materials in the recycling system for mechanical separation and metallurgical operations in a different way, similar to the model discussed in Chapter 8. The transformation of the liberation classes l due to the shredding operation is defined in the model based on a transformation matrix. The modelling of the different unit operations within the recycling flowsheet is discussed below.

Formulation of model for shredding

The transition of the liberation class distribution due to the shredding operation is defined in the model based on a shredding transformation matrix. This is similar as defined by Reuter and Van Deventer [309] for milling and flotation plants. It is possible to define a transformation matrix for the transition of the liberation class distribution over shredding Sf_i^{m,l_f,l_y}, where l_f is the liberation class of the feed f, whereas l_y is defined for the output y. The assumption has been made that all minerals m defined as Al (cast & wrought), Fe, Cu and rest based minerals (i.e. minerals A to E), break according to the same shredding transformation matrix (for the particle size reduction). This is obviously a simplification, since the various materials will break differently due to their specific mechanical properties, joining method, design, complexity and require therefore different transformation matrices. Separate matrices can however be defined for each mineral, but this was not done in this model.

Mass balance over shredder A mass balance can be set up over the shredding operation, which describes the transition of the mass flow over the liberation classes l for each mineral m (Eq. 9.1 and Eq. 9.2). Since no separation takes place (the in- and output of the shredder are both defined as one stream distributed over the liberation classes) no separation efficiency equation for the shredding operation is defined.

$$\left(\sum_{l=1}^{l=5}\left(Sf_i^{m,l}\cdot C^{m,l,k}\right)\right)\cdot f_i^m-\left(\sum_{l=1}^{l=5}\left(Sy_i^{m,l}\cdot C^{m,l,k}\right)\right)\cdot y_i^m=0 \tag{9.1}$$

with

$$\sum_{l=1}^{l=5} Sy_i^{m,l}=1 \tag{9.2}$$

Table 9.1: Typical parameters for the phase model as used for simulations. Definition of: (a) input matrix(composition and construction of the car); (b) liberation matrix for shredding (Sf_i^{m,l_f,l_g}); (c) composition matrix of liberation classes ($C^{m,k,l}$) for mineral A; and also B to E (bold gives the name of the metal/mineral)

(a)

	Mineral (kg)				
Liberation class	A	B	C	D	E
Lib. class 1	15	30	250	700	25
Lib. class 2	0	0	0	0	0
Lib. class 3	0	0	0	0	0
Lib. class 4	0	0	0	0	0
Lib. class 5	0	0	0	0	0

(b)

Shredding matrix (Sf_i^{m,l_f,l_g})

	Lib. class 1 (l_f)	Lib. class 2 (l_f)	Lib. class 3 (l_f)	Lib. class 4 (l_f)	Lib. class 5 (l_f)
Lib. class 1 (l_g)	0	0	0	0	0
Lib. class 2 (l_g)	0.01	0.01	0	0	0
Lib. class 3 (l_g)	0.1	0.05	0.05	0	0
Lib. class 4 (l_g)	0.1	0.05	0.05	0.05	0
Lib. class 5 (l_g)	0.79	0.89	0.9	0.95	1

(c)

Definition of liberation classes $C^{m,k,l}$

Mineral *A*	**Al wrought**	Al cast	Fe	Cu	Rest
Lib.class 1	0.60	0.20	0.10	0.05	0.05
Lib.class 2	0.70	0.15	0.10	0.03	0.02
Lib.class 3	0.75	0.10	0.10	0.03	0.02
Lib.class 4	0.95	0.05	0	0	0
Lib.class 5	1	0	0	0	0
Mineral *B*	Al wrought	**Al cast**	Fe	Cu	Rest
Lib.class 1	0.30	0.50	0.10	0.05	0.05
Lib.class 2	0.25	0.65	0.05	0.03	0.02
Lib.class 3	0.10	0.75	0.10	0.03	0.02
Lib.class 4	0.05	0.95	0	0	0
Lib.class 5	0	1	0	0	0
Mineral *C*	Al wrought	Al cast	Fe	Cu	**Rest**
Lib.class 1	0.02	0.02	0.06	0.1	0.8
Lib.class 2	0.02	0.02	0.04	0.07	0.85
Lib.class 3	0.02	0.02	0.03	0.03	0.9
Lib.class 4	0.015	0.015	0.01	0.01	0.95
Lib.class 5	0	0	0	0	1
Mineral *D*	Al wrought	Al cast	**Fe**	Cu	Rest
Lib.class 1	0.01	0.01	0.8	0.08	0.1
Lib.class 2	0.005	0.01	0.855	0.06	0.07
Lib.class 3	0.005	0.005	0.91	0.05	0.03
Lib.class 4	0.005	0.005	0.95	0.02	0.02
Lib.class 5	0	0	1	0	0
Mineral *E*	Al wrought	Al cast	Fe	**Cu**	Rest
Lib.class 1	0.01	0.01	0.03	0.8	0.15
Lib.class 2	0.005	0.005	0.02	0.85	0.12
Lib.class 3	0.005	0.005	0.01	0.9	0.08
Lib.class 4	0	0	0.01	0.95	0.04
Lib.class 5	0	0	0	1	0

Formulation of model for mechanical separation

Mass balance over mechanical separation The mass balance for mechanical separation is based on the defined minerals m and liberation classes l over the unit operations i and j (see Eq. 9.3).

$$f_i^{m,l} + \sum_{j=1}^{n} \alpha_{ij} x_j^{m,l} - x_i^{m,l} - y_i^{m,l} = 0 \tag{9.3}$$

Separation efficiency of mechanical separation processes (recovery based modelling) Since the liberation model describes recycling performance based on material properties, the separation efficiency of the mechanical recycling is defined in terms of only recovery and not in more complicated terms of grade/recovery curves (see Eq. 9.4).

$$(1 - Ry_i^{m,l}) \cdot y_i^{m,l} - Ry_i^{m,l} \cdot x_i^{m,l} = 0 \tag{9.4}$$

Formulation of model for metallurgical processing

A mass balance describes the material flows in metallurgical processing in which the relation between in- and output is given by the recovery for each of the different elements k present in the input for the melting furnace. The mass balance as well as the separation efficiency (recovery) of the metallurgical operations can be described in one equation (see Eq. 9.5). For the mass balance and separation efficiency for metallurgical processing the following equations (Eq. 9.5, Eq. 9.6 and Eq. 9.7) may be derived, representing respectively the mass balance and separation for stream y_i^k, x_i^k and z_i^k.

$$\left[\sum_{m=1}^{m=5}\left(\sum_{l=1}^{l=5} f_i^{m,l} \cdot C^{m,l,k}\right)\right] \cdot Ry_i^k - y_i^k = 0 \tag{9.5}$$

$$\left[\sum_{m=1}^{m=5}\left(\sum_{l=1}^{l=5} f_i^{m,l} \cdot C^{m,l,k}\right)\right] \cdot Rx_i^k - x_i^k = 0 \tag{9.6}$$

$$\left[\sum_{m=1}^{m=5}\left(\sum_{l=1}^{l=5} f_i^{m,l} \cdot C^{m,l,k}\right)\right] \cdot Rz_i^k - z_i^k = 0 \tag{9.7}$$

where:

$$Ry_i^k + Rx_i^k + Rz_i^k = 1 \tag{9.8}$$

Eq. 9.5, Eq. 9.6 and Eq. 9.7 calculate the fraction of each element k (Al wrought, Al cast, Steel, Cu and rest) present in each mineral class m of the input stream $f_i^{m,l}$ of metallurgical processing for the sum of all liberation classes l and composition matrix $C^{m,k,l}$. The mass flows of the elements k (Al wrought, cast etc.) present in each mineral m are determined from the calculated fractions by multiplication the fractions with the mass flow of the input stream for each mineral m $f_i^{m,p}$. A transition from mineral m to element k is being made by adding up element k over all mineral classes m (mineral A becomes Al wrought, mineral B Al cast, etc.). The mass balance and separation efficiency over the metallurgical processing for each of these elements k is calculated based on the recovery values Ry_i^k, Rx_i^k and Rz_i^k as given in the model. Since in the output of metallurgical processes the definition of liberation classes make no sense, the recovered elements k are added up over all liberation classes l or just simply alloy classes, the output y^k, x^k and z^k are only defined per element k. Therefore Eq. 9.5, Eq. 9.6 and Eq. 9.7 define the mass balance on element basis and not on mineral basis. The recovery values Ry_i^k, Rx_i^k and Rz_i^k can be a fixed value or can be dependent on the concentration of e.g. contaminants in the feed stream. The recovery value is then represented by (Eq. 9.9 and Eq. 9.10):

$$Ry_i^k - (a_p \cdot If_i^{k_{rest}}) - b_p = 0 \tag{9.9}$$

where:

$$k_{rest} = rest$$
$$If_i^{k_{rest}} = \sum_{m=1}^{m=5} \left(\sum_{l=1}^{l=5} f_i^{m,l} \cdot C^{m,k_{rest},l} \right) \tag{9.10}$$

where $If_i^{k_{rest},l}$ is e.g. the organic content of the aluminium fraction being the input of the metallurgical process, and a_p and b_p are plant parameters (where b_p is equal to the recovery value for a certain size class p as given in the matrix) that define the variation of recovery as a function of $If_i^{k_{rest},l}$. The same applies to Rx_i^k and Rz_i^k.

The recovery values for metallurgical processing are not defined as being dependent on the liberation class. The influence of liberation on the final metal recovery is taken into consideration by including the influence of the other elements, such as organics (=rest stream).

9.2.3 Flowsheet of the model

A simplified flowsheet (Figure 9.2) has been derived from the detailed recycling flowsheet for ELV's (Figure 8.3 [324]). This flowsheet forms the basis for the recycling optimization model for aluminium recycling as discussed here. Since the model focuses in particular on the optimization of aluminium, the metallurgical processing of aluminium is described in the model. The model has been developed in Microsoft® Excel and AMPL (see Appendix C.2).

9.2.4 Parameterisation of the recycling optimization model

As discussed above as well as in the previous chapters (Chapter 7 and 8) the recycling of the car is dependent on various parameters. Most of these parameters will change over time, such as the lifetime of the car, the weight and the composition, (implying the mineralogy) of the car. In Chapter 8 the development of a dynamic model was described, which predicts the behaviour of the resource cycle system over time, based on various distribution functions describing the statistic and time-varying nature of the mentioned parameters [51]. The recycling optimization model predicts the recovery rate of the various materials dependent on these time-varying parameters (design influencing liberation, separation efficiency, etc.). This section will discuss how various parameters were determined for the recycling optimization model.

Influence of the choice of materials in the design on the recycling

During the design stage, fundamental choices about a product are made, which have to satisfy product requirements for the different stages of its life cycle (production, use and recycling). As mentioned, design decisions on the product mineralogy (material combinations and connections) are of significant influence on the end-of-life phase of the product. Liberation of materials is never perfect during the shredding of the car. The combination of materials and in particular the way they are connected in product design will affect the degree of liberation,

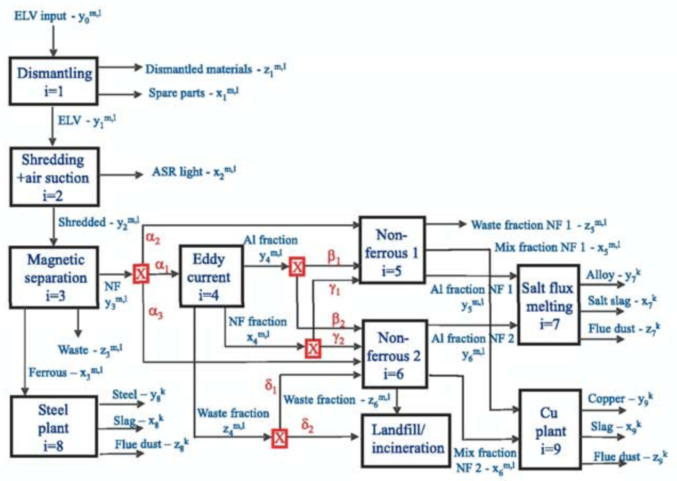


Figure 9.2: Simplified flow sheet for recycling ELV's, with $m = A$ - Al wrought based mineral, B - Al cast based mineral, C - remainder based mineral, D - steel based mineral, E - copper based mineral; k = elements Al wrought, Al cast, rest, steel, Cu; liberation class l = 1 to 5; i=plants, unit operations, transport, etc., with i= 1 to n; and α, β, γ and δ structural parameters [6]

the composition of the material streams after shredding and mechanical separation, and the amount as well as the composition of the non-liberated particles. Consequently mineralogy and liberation will affect the possibilities of material recovery as well as the recycling rate of the product. The material stream produced by the shredder consists of a complex mixture of materials, which are present as liberated (pure) and non-liberated (contaminated) particles. The materials in the stream have to be separated by mechanical recycling in order to create high quality material flows for the various elements (materials) present in the car. This will however lead to losses within in the different material cycles, since based on the interrelation between grade and recovery of a mechanical separation process, it can be concluded that the recovery of materials will always be lower than 100%, if the quality of recycled materials has to be increased by mechanical separation. However, the different materials locked up within the non-liberated particles can never be separated from each other by mechanical separation. A high quality feed is a prerequisite for producing high quality metal products after (s)melting, the recovery of which is constrained by the prevalent thermodynamics and kinetics. The contaminations present may lead to a degradation of material properties and moreover to the loss of valuable materials.

Material combination matrix

In order to apply a systematic approach to select desired and avoid problematic material combinations in product design and intermediate recycling products, a decision tree was developed, based on the separation and recycling technologies available nowadays and on metallurgical and thermodynamic properties of the materials [299, 335]. The decision tree is shown in Figure 9.3 and is self-explanatory. This decision tree must be read in conjunction with a selection matrix (Figure 4.9) describing which metal combinations are desirable for recycling and which are not. For example the matrix highlights the sensitivity of the lightweight metals (here aluminium and magnesium alloy families) to contaminants. It means that these metals should either be dismantled from the end-of-life product, carefully separated by mechanical processes, or the contamination of these materials with others should be avoided in product design. In Figure 4.9, also the components of an average passenger car, described by Castro et al. [336], are analysed, as an example of application of the matrix. The data behind Figure 4.9 on the limitations of contaminations in the input for metallurgical processing are included in the simulation model by imposing constraints on the output composition of the mechanical separation units (being the feed for metallurgy). Only three categories to control the input of metallurgical processes are distinguished, which can be translated to the model by eliminating the presence of unwanted components on the input composition of metallurgical processes by constraints on the system (red category). For the green category no restrictions have to be imposed onto the model. However a more detailed approach is required to describe the yellow category. Based on the prevalent thermodynamics and kinetics of the metallurgical processes (on the basis of which Figure 4.9 has been developed), fixed constraint values (or ranges) for the percentage of different contaminants allowed in the feed stream, can be included in the model. The matrix can be expanded by other materials. Lemmers [337] studied the compatibility of polymers for mechanical recycling. In summary this matrix determines the constraints on the various mineral and class flow rates as well is used to estimate the liberation classes and liberation matrix as described by Table 9.1.

Graedel and Allenby [39] discuss that pure metals are supremely recyclable, but that metals recycling is complicated by the use of mixed metals from different basic extraction processes. Graedel and Allenby [39] show the metals that commonly occur together and for which common extraction and purification processes have been developed. This is described

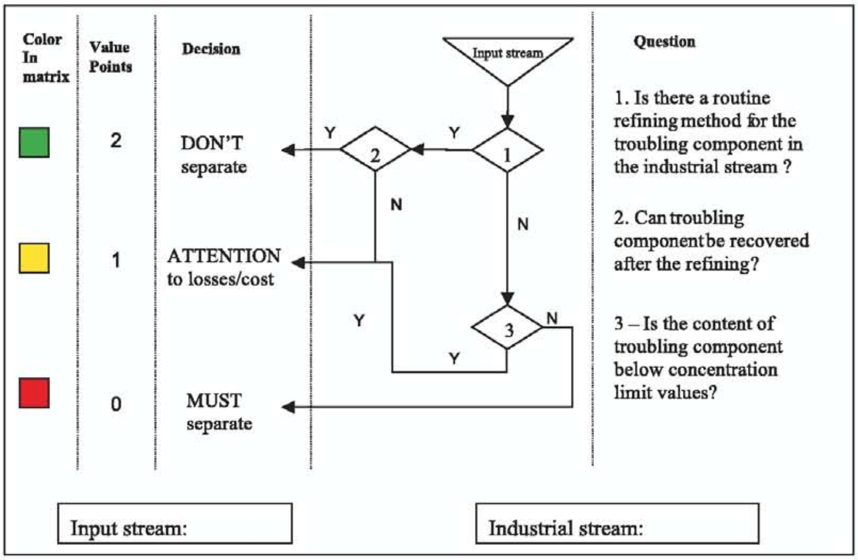


Figure 9.3: Decision tree for the selection of metal combinations during design interacting with Figure 4.9, which directly affect the liberation classes in Table 9.1. This has been developed for the average passenger car analysed on present material combinations in various car parts [335]

and modelled in much more detail by Verhoef et al. [7], showing the interconnectedness of the various metal cycles (see Figure 1.2). Instead of simply avoiding the mixing of material streams, the knowledge on possible (beneficial) material combinations as well as on problematic combinations is required in design for recycling, as also illustrated by Figure 4.9. This emphases the crucial importance of the recycling optimization model as developed in this Part (and recycling practice) to be able to calculate and control the grade of the recycling (intermediate) products.

9.2.5 Simulations on the optimization of product design, liberation and metallurgy

The recycling optimization model calculates the recovery of the different elements present in the car dependent on the objective of the optimization. The examples below will present the results of the recycling optimization model in particular for the optimization of the recycling of aluminium in the car. The simulations will show the interrelation of car design (product mineralogy), liberation and the quality of the intermediate recycling products, as well as their influence on material recovery (in particular for aluminium). The various simulations and their results will be described below.

Data for the recycling optimization model

The values for separation efficiencies (recovery values for model constraints as described above) are derived from experimental and industrial data as far as available. Since most of the data on the performance of the various unit operations appear to be incomplete or even lacking, estimation for the process efficiencies had to be made. As mentioned the same applies for the description of the composition of the liberation classes, which have never been measured up till now. Data have been collected by sampling and analyzing from industrial experiments and shredder plants. The theoretical, model based approach lays down a solid framework for data collection when setting up or performing recycling experiments. It makes clear what type of data have to be collected on different steps in the recycling of products, in order to describe and optimise the recycling of end-of-life vehicles, and in particular the inseparable link between product design and mineralogy, liberation, mechanical separation and metallurgical recovery. These fundamental insights on the importance of proper collection of data and the corresponding statistics and how this should be performed when carrying out experiments or auditing a plant have been lacking up till now! The data assumptions made in the model affect neither the usability of the system approach used to describe and optimise recycling systems nor the validity and applicability of the developed model as discussed above, since the model is based on prevailing mass balance and separation efficiency equations. Data assumptions only replace the calibration of the parameters and composition matrices in the model.

Software for optimization

For the optimization of aluminium recycling in ELV's, as discussed here, more than 400 variables with regard to the different material streams are defined. Furthermore, 9 variables describing the structural parameters α_{ij} are added (values α_1, α_2, α_3, β_1, β_2, γ_1, γ_2, δ_1, δ_2 in Figure 9.2) in order to optimise the structure of the network [51]). The software application used to perform this optimization is Frontline Systems' Premium Solver Platform, extended with the Large-Scale GRG Non-linear Solver [328], implemented in Microsoft®Excel [327], which is capable of handling this large scale, complex, non-linear optimization problem. The recycling optimization model as programmed in Microsoft® Excel and AMPL is depicted in Appendix C.2.

Definition of simulations

Various simulations have been performed in order to illustrate the influence of product design (material connections and combinations), liberation, on mechanical recycling performance and metallurgical recovery as discussed above. The objective for all of the simulations is to maximise the recovery of the aluminium minerals (A and B) coming from mechanical processing, while minimising the other mineral flows (C, D and E) in order to optimise the quality of the produced aluminium alloy, this according to Figure 4.9. The various simulations will vary the different parameters in the link between design, liberation and metal recovery in order to illustrate the role of each parameter separately in the recovery of materials from the car and the achieved product quality.

Base case scenario (simulation 1) The first simulation (simulation 1) optimises the recovery of mineral A and B (while minimising the others) based on a defined input definition of the car, a liberation matrix for shredding and the definition for the composition of the various liberation classes for the different minerals in the car. This simulation serves as the base case scenario, to which the results of the other simulations will be compared. Table 9.2 depicts the settings of the model for the first simulation.

Liberation (simulations 2 and 3) As discussed above the liberation of materials is directly related to the recovery of materials, since it determines the purity (or impurity) of the material streams in the recycling flowsheet. The influence of liberation is simulated in the model by defining different values for the liberation matrix for shredding in the model. The results of these simulations are presented in simulation 2 (increased liberation) and simulation 3 (decreased liberation). Table 9.2 represents the changed liberation matrices for shredding.

Material combinations in the car (simulation 4 and 5) Based on the matrix of Figure 4.9, design choices can be made to avoid unwanted material combinations in the design of the product. Redefining the composition of the various liberation classes simulates the effect of these design choices, e.g. less Fe is present in the various liberation classes of the Al containing minerals (*A* and *B*) (simulation 4). Table 9.3 gives the changed definition of the composition of the liberation classes for all minerals. In simulation 5, it is assumed that the particles are completely liberated (perfect design). In the definition of the liberation classes, all classes for a mineral will only consist of its main component (mineral *A* contains 100% Al-wrought in all classes, mineral *B* contains 100% Al-cast in all classes, etc.).

Table 9.2: Definition of liberation matrix for shredding for simulation 2 (a) and simulation 3 (b)

	Shredding matrix									
	Class1		Class2		Class3		Class4		Class5	
	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
Class 1	0.05	0	0	0	0	0	0	0	0	
Class 2	0.01	0.05	0.01	0.01	0	0	0	0	0	0
Class 3	0.05	0.10	0.05	0.05	0.05	0.05	0	0	0	0
Class 4	0.05	0.20	0.05	0.05	0.05	0.05	0.05	0.05	0	0
Class 5	0.89	0.60	0.89	0.89	0.9	0.9	0.95	0.95	1	1

Construction of the car (simulation 6) The data from Figure 4.9 can also be applied to change the construction of products. The influence of a decrease in connected materials in the design of the car on the final material recovery and on the output quality of the end product is simulated by defining the input of the recycling optimization model over more liberation classes (simulation 6). Table 9.4 describes the changed input definition.

9.2.6 Simulation results

The results for the various simulations are described below. The objective function for all the simulations is to maximise the recovery of the aluminium minerals (*A* and *B*) coming from mechanical processing, while minimising the other mineral flows (*C*, *D* and *E*) in order to optimise the quality of the produced aluminium alloy. The defined recovery constraints (upper and lower limits) will remain constant for the various simulations. For each of the simulations, the changed settings are given above. For all the simulations, the boundary condition on the Al content in the produced alloy was defined to be at least 85.0%. Table 9.5 shows the results of the various simulations.

The recovery of mineral *A* and *B* (recovery from mechanical separation) is given, being the objective of the optimization. Mechanical separation operates on the optimization of mineral recovery. The recovery of the element aluminium (over the whole flowsheet) is depicted as well, which shows completely different values from the recovery on mineral basis, due to incomplete liberation. When maximising the recovery of minerals (*A* and *B*) coming from mechanical

Table 9.3: Definition of composition of liberation classes for simulation 4.

Definition of liberation classes $C^{m,k,l}$					
Mineral *A*	**Al wrought**	Al cast	Fe	Cu	Rest
Lib.class 1	0.60	0.20	0.10	0.05	0.05
Lib.class 2	0.70	0.15	0.10	0.03	0.02
Lib.class 3	0.75	0.10	0.10	0.03	0.02
Lib.class 4	0.95	0.05	0	0	0
Lib.class 5	1	0	0	0	0
Mineral *B*	Al wrought	**Al cast**	Fe	Cu	Rest
Lib.class 1	0.30	0.50	0.10	0.05	0.05
Lib.class 2	0.25	0.65	0.05	0.03	0.02
Lib.class 3	0.10	0.75	0.10	0.03	0.02
Lib.class 4	0.05	0.95	0	0	0
Lib.class 5	0	1	0	0	0
Mineral *C*	Al wrought	Al cast	Fe	Cu	**Rest**
Lib.class 1	0.02	0.02	0.06	0.1	0.8
Lib.class 2	0.02	0.02	0.04	0.07	0.85
Lib.class 3	0.02	0.02	0.03	0.03	0.9
Lib.class 4	0.015	0.015	0.01	0.01	0.95
Lib.class 5	0	0	0	0	1
Mineral *D*	Al wrought	Al cast	**Fe**	Cu	Rest
Lib.class 1	0.01	0.01	0.8	0.08	0.1
Lib.class 2	0.005	0.01	0.855	0.06	0.07
Lib.class 3	0.005	0.005	0.91	0.05	0.03
Lib.class 4	0.005	0.005	0.95	0.02	0.02
Lib.class 5	0	0	1	0	0
Mineral *E*	Al wrought	Al cast	Fe	**Cu**	Rest
Lib.class 1	0.01	0.01	0.03	0.8	0.15
Lib.class 2	0.005	0.005	0.02	0.85	0.12
Lib.class 3	0.005	0.005	0.01	0.9	0.08
Lib.class 4	0	0	0.01	0.95	0.04
Lib.class 5	0	0	0	1	0

Table 9.4: Definition of total input 1025 kg (composition and construction) of the car for simulation 6.

	Mineral (kg)				
Liberation class	*A*	*B*	*C*	*D*	*E*
Lib. class 1	5	10	100	400	5
Lib. class 2	5	10	50	200	5
Lib. class 3	5	10	50	100	5
Lib. class 4	0	5	50	0	5
Lib. class 5	0	0	0	0	0

Table 9.5: Simulation results

	Recovery mineral A+B (%)	Recovery Al (%)	Al content in alloy (%)	Input primary Al (kg)
Simulation 1	93.9	60.6	85.4	
Simulation 2	94.3	61.6	86.1	
Simulation 3	91.3	57.3	85.0	3.4
Simulation 4	93.9	70.1	86.0	
Simulation 5	93.9	92.9	87.0	
Simulation 6	94.2	66.6	86.0	

processing, while minimising the other mineral flows (C, D and E) aluminium will be lost in these mineral streams. Moreover the Al content of the produced alloy is given to illustrate the influence of changes in product design and liberation on the final alloy quality (which is obviously influenced by the objective of the optimization as well, which was however the same for all simulations). The results for the various simulations give a clear indication of the influence of the various parameters on the results of recycling. The results are discussed below briefly for the different simulations.

- Simulation 1 is the base case scenario. For the given objective function and constraints imposed on the model (and the parameters as defined in Table 9.1) the recovery of mineral A and B, the aluminium recovery as well as the aluminium content of the produced alloy is calculated. The results of the other simulations due to changing liberation and design parameters will be compared to this simulation.

- In simulation 2, the liberation of the minerals during shredding was improved by changing the shredding matrix (see Table 9.2). Simulation 2 clearly indicates that an increased liberation will lead to a higher mineral recovery (since the recovery of the more liberated particles is defined as being higher in the model). The final aluminium recovery increases and consequently an improvement in alloy quality can be observed.

- Simulation 3 illustrates the opposite. Due to decreased liberation of the materials, the recovery of the minerals A and B is decreasing, as well as the aluminium recovery. Obviously this trend can be observed in the output alloy composition as well. In this simulation, it was necessary to add primary aluminium in order to comply with the required constraint on the aluminium content of the alloy.

- Simulation 4 shows the result for a better-designed product; in which undesired material combinations were reduced. As can be expected, this will be of no influence on the mineral recovery. However, the recovery of aluminium increases significantly. The output alloy composition also shows increased aluminium content.

- The same applies for simulation 5. In this simulation, the recovery of aluminium increased to almost the same value as the mineral recovery, due to the completely liberated particles. The small difference between mineral and aluminium recovery is caused by a small amount of organics present in the input for the metallurgical plant, due to imperfect mechanical separation, causing losses. The recovery has however not reached a value of 100% due to the limitations of mechanical separation and losses during the metallurgical smelt operation.

- Due to the decrease in material connections in the design (input defined over more liberation classes) both the mineral as well as the aluminium recovery show an increased value in simulation 6. Consequently, this results in a higher purity of the produced alloy.

9.3 Modelling of particle size reduction and liberation in recycling of ELV's

Models for the simulation and optimization of the recycling of passenger vehicles have been developed as discussed in Chapter 8 and in the previous paragraphs [51, 338] on the basis of particle size and liberation classes respectively. The first recycling optimization model discussed in Chapter 8 [51] defines the (separation of the) material streams based on particle size classes p and elements k (k = Al wrought, Al cast, Rest, Steel, Cu). The second model as discussed in the previous paragraphs [338] describes the material streams in terms of m minerals A to E (representing respectively Al-wrought, Al-cast, Rest, Steel and Cu based metals/minerals) and l liberation classes. The degree of liberation of a product is described by defining for each of the minerals A to E the fraction of the various elements k present in the particles of the material flows within the different liberation classes l. In the first model the separation efficiency of the various physical separation steps is defined in terms of grade/recovery curves, whereas the second model describes the separation in terms of recovery only. The grade (based on metals/minerals m) and the exact composition of the streams (based on the elements k) can be calculated from the model. What is to date not been modelled for recycling systems is the combination of particle size distribution (size classes) and liberation classes in one model to investigate the interrelation between product design and recycling rate. Although the first and second model in a simplified manner disconnected particle size and liberation and therefore could give an indication of recycling rate, the mentioned combination gives a truer formulation of reality. The third model, which will be discussed in the next section, combines both the particle size and liberation. This approach also gives a good insight into what the breakage matrix for liberation looks like, revealing that classical minerals processing thinking cannot be applied directly to recycling systems [6].

9.3.1 Design for recycling and design for environment

Design for recycling and design for environment are the topic of many studies in literature as well as in industry. Graedel and Allenby [39] discusses that the concept of Industrial Ecology is one in which the cyclization of materials at their highest possible purity and utility level is of highest importance. This cyclization can only occur if materials from products that have reached the end of their useful life reenter the industrial flow stream and become incorporated into new products [39]. Graedel states that the efficiency with which cyclization occurs is highly dependent on the design of products and processes; it thus follows that designing for recycling (DfR) is one of the most important aspects of industrial ecology . It is discussed that Design for Recycling (DfR) should focus on a small number of rules defined by Graedel as given below[39, 40]:

- minimise the use of materials;
- minimise the materials diversity, i.e. the number of different materials used;
- choose desirable materials, considering manufacturing, use characteristics, and recycling;
- make it modular;

- make it efficient to disassemble;
- make it easy to recover.

These simple rules are part of many studies and discussions on Design for Recycling e.g. by Henstock [43], and Keoleian et al. [42] and have also been adopted by automotive industry [44, 45], although the latter focus in particular on design for dismantling. This will however lead only to a very small improvement in the recyclability; since dismantling is only beneficial to a certain extend due to its high labour costs. Design for Recovery has also been part of a EUCAR program (European council for automotive R&D) [339], which discusses design for recovery guidelines based on a combination of dismantling, shredding and PST processing (post shredding technology). Coppens et al. [340] discusses a design for recycling software tool developed by PSA Peugeot-Citron . This DFR methodology (software) focuses on dismantling. Although the design for recycling or design for recovery rules (e.g. EUCAR [339]) presented could be in principle correct, these are not supported by detailed knowledge of the behaviour of the recycling system and its material flows and will therefore never result in the total optimization of recycling based on improved design. The detailed technological knowledge, which is required to capture the complex interaction of processes and material and energy flows within the interconnected recycling system is lacking in these approaches. The crucial role of the quality of recycling (intermediate) products in the realisation of high recycling rates as well as the role of product design and its complex interaction with the liberation and recycling of end-of-life vehicles is not addressed. This implies that recycling cannot be optimised something that is often suggested in these studies without a fundamental basis. Design for recycling can never be realised, when the technological framework of recycling is represented in a too simplified manner and will therefore only result in very general and trivial guidelines. A comprehensive overview of the methods and tools supporting Design for Recycling/Environment is given by Bullinger [341]. Bullinger distinguishes three different categories in the existing tools: (1) literature/events, such as standards, guidelines, consulting, etc.; (2) conventional means of support in which a distinction can be made between tools focused on disassembly and materials (material compatibility matrices) and holistic tools; and (3) computer based means of support, focused on either disassembly, materials or on a holistic solution. However these methods are not supported by a sound technological and mathematical basis optimising the total recycling system (and not just dismantling orientated) in close link to the design of the product, e.g. the material compatibility matrices are not included in a the discussed recycling tools, linking liberation, separation efficiency to the grade of the intermediate recycling streams produced as is done in this Part. Only then the use of a material compatibility matrix makes sense. Most of the computer based tools are focused on design for environment, in which a solid technological description of the recycling system and its complex interaction to the design of the car is lacking. A design for recycling tool, Ecoscan-Dare has been developed by TNO [342]. This tool focuses mainly on WEEE (Waste from Electronic and Electronical equipment) and calculates environmental impact scores on the basis of the Eco-indicator '99 methodology. Although some technological insights in the recycling system are integrated in this tool, it does not capture the crucial role of liberation in relation to separation efficiency and recycling rate, making its application for design for recycling therefore debatable. Nagel and Meyer [343] discuss a method for systematically analysing and modelling end-of-life networks. However, this method, which focuses mainly of waste of electronic and electrical equipment (WEEE), covers in principal only the logistics of take-back schemes for WEEE, which is not really translated into a model. Any technological data on end-of-life processing (and process networks) is not included in the approach, although this plays a crucial role, also in view of the logistics of recycling networks. The recycling optimization models as presented in this Part, which has its focus on the recycling phase, in relation to the dynamics of the resource cycle, could be adopted by Design for Recycling approaches and could fill in this lack of detail based on technological knowledge of recycling systems. This could lead to the improvement and refinement of Design for Recycling within Industrial Ecology and the automotive industry. Furthermore, by placing this work into a larger framework as e.g. described by Industrial Ecology (design for) recycling, based on a fundamental basis, would be placed into the broader scope of Design for Environment, in which the total life cycle impact is addressed. Although Graedel emphasis the effect of fastening parts together in the design of the car, this is only done from the perspective of efficient disassembly. The fastening of parts and combination of materials have not been linked to shredding, liberation and therefore the separation efficiency and quality of recycling (intermediate) products.

9.3.2 Particle liberation modelling of ELV's in relation to minerals processing

The particle size reduction and the liberation of materials during shredding, which is among others determined by product design, will both affect the recycling of end-of-life products as is indicated by the two different models as discussed [51, 338]. This is a well known fact from minerals processing technology [334]. In order to define the effect of both particle size and liberation on the separation efficiency, the composition of the intermediate recycling streams and the final metal/material recovery, it is essential to combine these two parameters (particle size reduction and liberation) into one model, a fact that was not previously considered. Therefore, the two different models as discussed previously [51, 338] are combined into one final model, which includes the particle size reduction as well as the liberation of the materials to describe the influence of product design and material combinations and connections (mineralogy), particle size of the product and material flows, and liberation (product/particle composition) on the (optimization of) recycling end-of-life vehicles [6]. This model is developed using the knowledge available from the modelling and simulation of minerals processing systems [334] and integrating this into simulation models as defined by Reuter and van Deventer [309]. King [334] discusses the quantitative modelling of the unit operations of minerals processing, for which the modelling of particle size and liberation are essential. The modelling of both particle size and liberation is based on combined distributions as well as population balance methodology. The modelling is based on the definition of the distribution of particles in a size-composition space (matrix). Liberation is modelled only to the extent that is necessary to provide the link between comminution and mineral recovery. In spite of a difference in comminution behaviour of mineral ores compared to man-made products, the same principle for the definition of the relation between particle size and liberation (expressed as grade in minerals processing) can be applied to describe the particle size related to the liberation for the modelling of the comminution and separation of any end-of-life consumer product. It is discussed by King [334] that during comminution of mineral ores there is a natural tendency towards liberation and particles that are smaller than the mineral grains that occur in the ore can appear as a single mineral. This happens when the particle is formed entirely within a mineral grain, but is impossible when the particle is substantially larger than the mineral grains in the ore. However, King [334] discusses that the distributions of particles with respect to the composition do show some regular features particularly with respect to the variation of the distribution with particle size. This is however not necessarily the case for the comminution of modern consumer products of which the design and the related particle size reduction and liberation behaviour is much more complex than that of mineral ores. This is often the case due to the metals/mineral not being finely divided in the consumer products as is the case for geological ores. Due to the design and construction of the car it is difficult to define a grain size of the 'minerals'/elements in the product. The grain size of any metal/mineral in a modern consumer product such as the car is not defined by natural mineralogy, but by continuously changing design, composition, size and connection of the various elements created by man and can differ from car to car as well as over time. This implies that what is true for classical grinding i.e. the finer the grind the more liberated particles become is not necessarily true for shredding of end-of-life consumer goods. The models for liberation as described by King [334] are specific to mineralogical textures that consist of only two minerals - a valuable species and all the other minerals that are present and which are classified as gangue minerals. Although the techniques that are used can be applied to multi-component ores, King [334] discusses that the details of a suitable analysis are not yet worked out and are therefore not discussed. The modelling of the comminution of consumer products such as cars can however not be performed on a two component system, but requires the description of all (major) elements present in the car. Many elements building up the car have to be considered as economically valuable and/or environmentally relevant species. The contamination of one element flow, even with a low quantity of other elements, due to e.g. incomplete liberation could have direct implications for the final recovery rate to be achieved (e.g. the maximum concentration of Cu allowed in steel is 0.25%). It is discussed by Gay [344] that it is essential to model multi-phase particles, instead of binary particles on which most research effort in minerals processing has focused, since:

- particles are multi-phase;
- separation efficiency is determined by mineral association;
- particle breakage is not controlled by the mineral of interest but by the presence of all minerals.

It is clear that the same applies for the liberation of the various materials composing the car, for which most of the materials represent an economic value as well, this in contradiction to traditional minerals. Gay [344] defines the multi-phase particles as particle types, in which particles with very similar composition properties are grouped. Hence modelling is applied to particle types rather than individual particles. Metha [345] also developed a liberation model for multi-component minerals. However due to the fundamental difference in the breakage behaviour as well as the complexity of materials between minerals and complex time-varying consumer products such as the car, these models cannot simply be applied for the modelling of car recycling. Gay [344] discusses a liberation model for communication of multi-component particles based on probability theory to determine the relation between the feed and the product particles. Since the design of the car is in essence defined on a completely different basis than the car after shredding, consisting of liberated and un-liberated particles, it can be stated that modelling and predicting the relation between the feed 'particle', which is in fact the car, and the product particles is complicated and differs from modelling this relation for minerals and ores. In order to increase the degree of liberation, particles need to be broken as fine as possible [344]; however by decreasing particle size, energy costs substantially increase, and it becomes more difficult to separate particles. The same principle applies for the shredding of the car. There is a practical limitation to which the car can be shredded and particle size can be reduced, not only due to shredding process costs, but as well as due to a restriction of physical separation processes to process fine materials. In current recycling practice, the 0-10 mm fraction after shredding is in most plants still being land filled. The effect of particle size on the recovery (or particle throw) of non-ferrous metals is mentioned by Van der Beek et al. [346], Rem [347], Zhang et al. [348] and Maraspina et al. [349]. Moreover some types of joints cannot be destroyed by shredding (e.g. surface type connections such as hylite, Castro et al. [176]). Additionally, the degree of liberation of metal particles could also decrease during shredding due to the intensive plastic deformation these particles undergo in the shredder [350, 351]. As a consequence, materials that were not connected in the design can become attached in particles after shredding. This reveals the fundamental difference between the comminution of minerals, which are all brittle, and the shredding of cars, of which most of the materials or ductile. This leads to a fundamental difference in the breakage behaviour of minerals and consumer goods. In addition, a smaller particle size due to intensive shredding means an increase of particle specific surface area, what could lead to oxidation losses (decrease of metal yield) in reactive metals such as aluminium and magnesium [352]. As indicated by King [334], the simulation of multi-component/mineral liberation is difficult. This work and developed model attempts a first step into the direction of simulating multi-component/mineral liberation systems. The model remains on the system level and uses simplified liberation models.

9.3.3 Flowsheet of the model for recycling end-of-life vehicles

A simplified flowsheet (Figure 9.4) has been derived from the detailed recycling flowsheet for ELV's as depicted by Figure 8.4 [324]. This flowsheet forms the basis for the particle size and liberation based recycling optimization model as discussed here, and is also an expansion to the flow sheet discussed previously (above and in Chapter 8). This flowsheet includes not just the metallurgical processing of aluminium as was discussed in Chapter 8, but also of steel and copper. This makes it possible to include the recovery of all metals defined in the models, as well as their quality (of the in-and output of the metallurgical processes) in the modelling and optimization, as well as in the calculation of the recycling rate [6]. The flow sheet of Figure 9.4 is very similar to that of Figure 9.2, however the model includes the particle size classes and mixing operations in order to model both particle size and liberation.

9.3.4 Phase description of the model

Mineral classes (m)/Particle classes (p)

The mass (kg) of the material flows $y_i^{m,p}$ in the recycling flowsheet (Figure 9.4) is described in the model based on the minerals A to E, distributed over the defined particle size classes p (see Table 9.6(a)).

Element classes (k)/ Liberation classes (l)

For each of the particle size classes in a specific material flow $y_i^{m,p}$ a discrete 'distribution' of material over the liberation classes l =1 to 5 is defined in the liberation/particle size matrix $Ly_i^{m,p,l}$ (see Table 9.1(b)), which is in principle similar to the definition of the particle distribution in the size-composition space as discussed by King [334]. This matrix $Ly_i^{m,p,l}$ defines thus for each mineral m the fraction of material present in liberation classes l =1 to 5 for the different particle size classes p for the material stream y_i after each unit operation i. This matrix is also defined for the model input (being the car), describing in this way the particle size classes and liberation classes determined by the design of the car. The composition matrix $C^{m,l,k}$ defines for each mineral m the composition of the different liberation classes l for the elements k (see Table 9.6(c)) as discussed previously in this chapter [338]. Table 9.6(c)

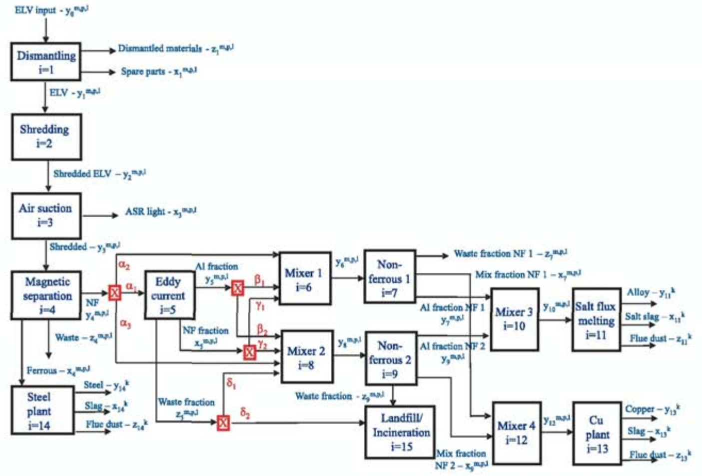


Figure 9.4: Simplified flow sheet for recycling ELV's, with $m = A$ - Al wrought based mineral, B - Al cast based mineral, C - remainder based mineral, D - steel based mineral, E - copper based mineral; k = elements Al wrought, Al cast, rest, steel, Cu; particle size class p = 1 to 5; liberation class l = 1 to 5; i =plants, unit operations, transport, etc., with i = 1 to n; and α, β, γ and δ structural parameters [6]

summarises an example for the definition of the composition of the liberation classes in the model for a mineral A (in this case a mineral with Al-wrought being the major component). Similarly there are minerals B (Al-cast rich), C (Plastic rich/rest), D (Steel-rich) and E (Cu-rich).

Table 9.6: Typical examples of the phase model as used for simulations for mineral A. Definition of: (a) mass based particle size distribution of the input ($y_i^{m,p}$); (b) liberation/particle size matrix $Ly_i^{m,p,l}$; (c) composition matrix of liberation classes ($C^{m,k,l}$) for mineral A; and also B to E (bold gives the name of the metal/mineral)

(a)

Particle size class	Mineral (kg) A	B	C	D	E
Part. size class 1	15	30	250	700	25
Part. size class 2	0	0	0	0	0
Part. size class 3	0	0	0	0	0
Part. size class 4	0	0	0	0	0
Part. size class 5	0	0	0	0	0

(b)

		Lib. cls. 1 (l_f)	Lib. cls. 2 (l_f)	Lib. cls. 3 (l_f)	Lib. cls. 4 (l_f)	Lib. cls. 5 (l_f)
A in ELV	Part. sz. cls. 1	0.200	0.200	0.200	0.200	0.200
A in ELV	Part. sz. cls. 2	0.000	0.250	0.250	0.250	0.250
A in ELV	Part. sz. cls. 3	0.000	0.000	0.333	0.333	0.333
A in ELV	Part. sz. cls. 4	0.000	0.000	0.000	0.500	0.500
A in ELV	Part. sz. cls. 5	0.000	0.000	0.000	0.000	1.000

(c)

Definition of liberation classes

Mineral A	**Al wrought**	Al cast	Fe	Cu	Rest
Lib. class 1	0.5	0.2	0.2	0.05	0.05
Lib. class 2	0.65	0.15	0.15	0.03	0.02
Lib. class 3	0.75	0.1	0.1	0.03	0.02
Lib. class 4	0.87	0.05	0.05	0.02	0.01
Lib. class 5	1	0	0	0	0
Mineral B	Al wrought	**Al cast**	Fe	Cu	Rest
Lib. class 1	0.2	0.5	0.2	0.05	0.05
Lib. class 2	0.15	0.65	0.15	0.03	0.02
Lib. class 3	0.1	0.75	0.1	0.03	0.02
Lib. class 4	0.05	0.87	0.05	0.02	0.01
Lib. class 5	0	1	0	0	0
Mineral C	Al wrought	Al cast	Fe	Cu	**Rest**
Lib. class 1	0.04	0.04	0.06	0.06	0.8
Lib. class 2	0.03	0.03	0.04	0.05	0.85
Lib. class 3	0.02	0.02	0.03	0.03	0.9
Lib. class 4	0.015	0.015	0.01	0.01	0.95
Lib. class 5	0	0	0	0	1
Mineral D	Al wrought	Al cast	**Fe**	Cu	Rest
Lib. class 1	0.01	0.01	0.8	0.08	0.1
Lib. class 2	0.01	0.01	0.85	0.06	0.07
Lib. class 3	0.01	0.01	0.9	0.05	0.03
Lib. class 4	0.005	0.005	0.95	0.02	0.02
Lib. class 5	0	0	1	0	0
Mineral E	Al wrought	Al cast	Fe	**Cu**	Rest
Lib. class 1	0.01	0.01	0.03	0.8	0.15
Lib. class 2	0.005	0.005	0.02	0.85	0.12
Lib. class 3	0.005	0.005	0.01	0.9	0.08
Lib. class 4	0	0	0.01	0.95	0.04
Lib. class 5	0	0	0	1	0

9.3.5 Alloy types

The output of the metallurgical processes has to comply with constraints on the alloy composition. Since each element is described separately in the composition matrices $C^{m,l,k}$ composing the various minerals, the output of the metallurgical operation can be calculated by adding all elements present in the various material flows, being the input for metallurgical processing (see Figure 9.4). This implies that elements must be added from the different size classes p, of which the composition is defined by combining the liberation/particle size matrix $Ly_i^{m,p,l}$ and the composition matrix $C^{m,l,k}$. The grade of mechanical separation can also be calculated from the model. Aluminium is described in the model as wrought or cast, each with its own specific (average) composition. To be able to calculate the produced alloy type, the composition of the wrought and cast aluminium is described in a separate alloy matrix in the model. Together with the contaminants or alloying elements ending up in the alloy, the exact alloy composition can be calculated from the model based on the degree of liberation and can be controlled by defining boundary conditions on the output i.e. the metal quality. Primary materials (aluminium and alloying elements) often have to be added to produce a required alloy composition due to losses in the system. These primary materials are defined as one of the input streams of the model. The addition of primary materials must be kept to a minimum, for economical and environmental reasons. This can be realised by including negative cost penalties to the primary materials in the objective function of the recycling optimization model.

9.3.6 Separation models

Since the performance of an unit operation is related to the particle size and degree of liberation of the feed of the processes, the separation can be defined for different ranges of size classes p and liberation classes l. The transformation matrices $Ty_i^{m,p,l}$, $Tx_i^{m,p,l}$ and $Tz_i^{m,p,l}$ (see the example in Table 9.7) define the recovery values for each mineral m for each particle size class p and liberation class l for mechanical separation processes i for respectively stream y_i, x_i and z_i. The difference in separation efficiency (recovery) is determined by the size class as well as the degree of liberation. However, the influence of the each individual material present in a non-liberated particle cannot be expressed in the recovery rate for mechanical separation (e.g. the presence of 10% Fe in Al will have another effect on the recovery rate for Eddy Current separation than the presence of 10% organic materials). An additional distinction should be made for the different material combinations possible in a certain liberation class to be able to model this. This is however not taken into consideration in the defined model in this chapter, but is an important issue.

Table 9.7: Example of a transformation matrix $Ty_i^{m,p,l}$ with the recovery values for each individual particle size class p and liberation class l defined for m = mineral A for separation process $i = 5$ (Eddy Current separation - Figure 9.4) flowing to the product stream y_i

$Ty_i^{m,p,l}$ (m = mineral A)						
		Lib. class 1	Lib. class 2	Lib. class 3	Lib. class 4	Lib. class 5
$i = 5$ Eddy Current	Part. sz. cls. 1	0.8000	0.8400	0.8800	0.9200	0.9600
	Part. sz. cls. 2	0.8000	0.8400	0.8800	0.9200	0.9600
	Part. sz. cls. 3	0.8000	0.8400	0.8800	0.9200	0.9600
	Part. sz. cls. 4	0.8000	0.8400	0.8800	0.9200	0.9600
	Part. sz. cls. 5	0.2000	0.2000	0.2000	0.2000	0.3000

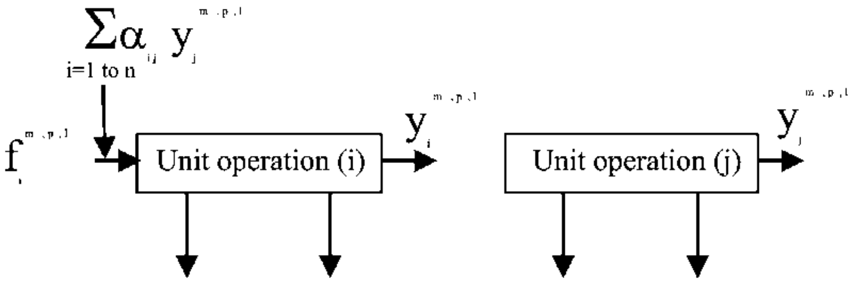


Figure 9.5: General overview of mass flows over unit operation i and j for each mineral m in a particle size class p and liberation class l

9.3.7 Formulation of the recycling optimization model

From the recycling flowsheet (Figure 9.4) four different types of processes can be defined viz. shredding, mechanical separation, mixing and metallurgical processing. Since these operations are fundamentally different, the model describes the flow of materials in the recycling system for these operations in a different way. The description of these unit operations in the recycling optimization model is discussed below in four separate sections. As discussed in Chapter 8 [51] two types of equations can in principal describe the flow of materials in the system of processes and the structure of the network for each individual mineral/element present in the car viz.:

- mass balance equations, including structural parameters for each mineral m, element k, particle class p, and liberation class l and;
- separation efficiency models for each of the unit operations for each mineral m, element k, particle class p, and liberation class l;

which are both based on:

- liberation distributions of liberation classes l for each mineral m and particle size class p and;
- the composition of each liberation class l based on elements k for each mineral m.

The various parameters playing a role in the efficiency of the material cycle (economy, legislation, etc.) can be translated into constraints imposed onto the model, the equations mentioned and an objective function for optimization. These theoretical equations comprise the basis of the model, giving the constraints imposed on the system. The material flows for the minerals m (defined based on elements k) in different size classes p and liberation classes l between the unit operations and interconnections between these processes as depicted in the recycling flow sheet of Figure 9.4 can be simplified and generalised as shown in Figure 9.5.

Formulation of model for shredding

The transition of the particle size as well as of the liberation class distribution within the particle size classes due to the shredding operation can be defined in the model based on shredding transformation matrices. This is similar as defined by Reuter and Van Deventer

[309] for milling and flotation plants. However the transitions of particle size and liberation class are defined in separate transformation matrices. It is possible to define a transformation matrix for the transition of the particle size distributions over shredding Sf_i^{m,p_f,p_y}, where p_f is the particle size class of the feed f, whereas p_y is defined for the output y. The assumption has been made that all materials defined as Al (cast & wrought), Fe, Cu and rest based minerals (i.e. minerals A to E), break according to the same shredding transformation matrix (for the particle size reduction). This is obviously a simplification, since the various materials will break differently due to their specific mechanical properties, joining method, design, complexity and require therefore different transformation matrices. Separate matrices can however be defined for each mineral, but this was not done in this model. Since no data is available on the transition of liberation class distributions during shredding no reliable definition for the shredding matrix for the liberation class transition could be presented here. Moreover, the definition of a liberation class transition matrix would require detailed insight into the relation between the particle size and liberation class transition, which is unknown for complex products such as cars. However the modelling of transition of the liberation class distribution can be described sufficiently based on a mass balance over the shredding operation for the elements k building up the liberation classes l as defined in the composition matrix for liberation $C^{m,l,k}$. The shredding matrix for particle size class transition is changing the distribution of the mass flow of the minerals m over the different particle size classes p after shredding. Therefore, the shredding matrix for the liberation class transition would change the definition of matrix $Lf_i^{m,p,l}$ to $Ly_i^{m,p,l}$ due to the shredding operation. It changes the distribution of liberation classes in the different particle size classes p for each mineral m.

Mass balance for shredding for $i = 2$ in Figure 9.4 (shredder - particle size reduction) A mass balance can be set up over the shredding operation, which describes the transition of the mass flow over the particle size classes p for each mineral m (Eq. 9.11 and Eq. 9.11). Since no separation takes place (the in- and output of the shredder are both defined as one stream distributed over the particle size classes) no separation efficiency equation for the shredding operation is defined.

$$\left(\sum_{p_y=1}^{p_y=5} Sf_i^{m,p_f,p_y} \cdot f_i^{m,p_f}\right) - y_i^{m,p_y} = 0 \tag{9.11}$$

with

$$\sum_{p_y=1}^{p_y=5} Sf_i^{m,p_f,p_y} = 1 \tag{9.12}$$

Liberation during shredding The shredding operation will change the definition of the liberation of the various minerals in the different particle size classes p as given in the particle size/liberation matrix $Lf_i^{m,p,l}$. The relation between the liberation class distribution of the in- and output of the shredder can be described by Eq. 9.13 and Eq. 9.14.

$$\sum_{p=1}^{p=5}\left(\sum_{l=1}^{l=5}(Lf_i^{m,p,l} \cdot C^{m,l,k})\right) \cdot f_i^{m,p} - \sum_{p=1}^{p=5}\left(\sum_{l=1}^{l=5}(Ly_i^{m,p,l} \cdot C^{m,l,k})\right) \cdot y_i^{m,p} = 0 \tag{9.13}$$

with

$$\sum_{l=1}^{l=5} Ly_i^{m,p,l} = 1 \tag{9.14}$$

Formulation of model for mechanical separation processes

Mass balance mechanical separation The mass balance equations define the flow of the material streams between the different unit operations and the structure of the network of processes. For the two unit operations i and j as represented in Figure 9.5 the mass balance constraint defined by Eq. 9.15, Eq. 9.16 and Eq. 9.17 may be derived. The mass balance for mechanical separation is defined here for a single input stream, since the mixing operation (see Figure 9.4) will transform a multiple input for mechanical separation into one stream and is therefore defined and modelled as a different process type. The mass balance for mixing must therefore hold for a multiple input stream (if the mixing step was not defined, this must also hold for mechanical separation).

$$f_i^{m,p} - y_i^{m,p} - x_i^{m,p} - z_i^{m,p} = 0 \tag{9.15}$$

and

$$f_i^{m,p} = \alpha_{ij} \cdot y_j^{m,p} \tag{9.16}$$

$$0 \leq \alpha_{ij} \leq 1 \quad \text{and} \quad \sum_{i=1}^{n} \alpha_{ij} = 1 \; for\, all\, j \tag{9.17}$$

Although in the model, the mass balance is calculated based on particle size classes, the mass balance over the mechanical separation must also close for the mass flows over both particle size and liberation classes. Since during mechanical separation no transformation of particle size classes as well as liberation classes will take place, the following mass balance equation (Eq. 9.18 to Eq. 9.21) also holds for mechanical separation:

$$f_i^{m,p,l} - y_i^{m,p,l} - x_i^{m,p,l} - z_i^{m,p,l} = 0 \tag{9.18}$$

and

$$f_i^{m,p,l} = \alpha_{ij} \cdot y_j^{m,p,l} \tag{9.19}$$

with

$$y_i^{m,p,l} = Ly_i^{m,p,l} \cdot y_i^{m,p} \tag{9.20}$$

and

$$\sum_{l=1}^{l=5} Ly_i^{m,p,l} = 1 \tag{9.21}$$

Separation efficiency of mechanical separation processes (recovery based modelling) The recovery of a mineral during mechanical separation is determined by both the influence of particle size as well as liberation on the separation efficiency. Therefore it is essential to describe the separation efficiency equation based on both particle size as well on liberation. Eq. 9.22 to Eq. 9.25 define the separation efficiency equations for mechanical separation in the model. The transformation matrices $Ty_i^{m,p,l}$, $Tx_i^{m,p,l}$ and $Tz_i^{m,p,l}$ (see Table 9.7) define the recovery values for each mineral m for each particle size class p and liberation class l for mechanical separation processes i for respectively stream y_i (Eq. 9.22), x_i (Eq. 9.23) and z_i (Eq. 9.24).

$$(1 - Ty_i^{m,p,l}) \cdot y_i^{m,p,l} - Ty_i^{m,p,l} \cdot x_i^{m,p,l} - Ty_i^{m,p,l} \cdot z_i^{m,p,l} = 0 \tag{9.22}$$

$$(1 - Tx_i^{m,p,l}) \cdot x_i^{m,p,l} - Tx_i^{m,p,l} \cdot y_i^{m,p,l} - Tx_i^{m,p,l} \cdot z_i^{m,p,l} = 0 \tag{9.23}$$

$$(1 - Tz_i^{m,p,l}) \cdot z_i^{m,p,l} - Tz_i^{m,p,l} \cdot y_i^{m,p,l} - Tz_i^{m,p,l} \cdot x_i^{m,p,l} = 0 \tag{9.24}$$

where:

$$Ty_i^{m,p,l} + Tx_i^{m,p,l} + Tz_i^{m,p,l} = 1 \tag{9.25}$$

During mechanical separation, the definition of the distribution of materials within particle size class p over liberation class l will change, due to the fact that for each mineral the recovery values can differ per particle size and liberation class. The defined particle size/liberation matrix will therefore change after each mechanical separation step, according to the defined recovery values in the transformation matrix for mechanical separation efficiency. The transformation of the particle size/liberation matrix $Ly_i^{m,p,l}$ due to redistribution of the material streams during mechanical separation is defined by Eq. 9.26.

$$\frac{Ty_i^{m,p,l} \cdot Lf_i^{m,p,l}}{\sum_{l=1}^{l=5}(Ty_i^{m,p,l} \cdot Lf_i^{m,p,l})} = Ly_i^{m,p,l} \tag{9.26}$$

where: $Lf_i^{m,p,l}$ is the particle size/liberation matrix of the feed stream $f_i^{m,p,l}$ of unit operation i (see Figure 9.5). Dividing by the summation in Eq. 9.26 is required to normalise the particle size/liberation class distribution. Similar equations hold for the streams $x_i^{m,p,l}$ and $z_i^{m,p,l}$.

Formulation of model for mixing

A mixer is being defined in the model in order to convert multiple input streams, with each their own corresponding particle size/liberation matrix $Lf_i^{m,p,l}$ to one stream, with its corresponding new particle size/liberation matrix, determined by the ratio between the various input streams. The mass balance holding for the mixing unit operations is given by Eq. 9.27 and Eq. 9.28.

$$F_i^{m,p} - y_i^{m,p} = 0 \tag{9.27}$$

where:

$$F_i^{m,p} = f_i^{m,p} + \sum_{j=1}^{n} \alpha_{ij} \cdot y_j^{m,p} \tag{9.28}$$

Since no transformation of particle size and liberation classes takes place during mixing, the following equation can also be defined for the mixing operation (Eq. 9.29):

$$F_i^{m,p,l} - y_i^{m,p,l} = 0 \tag{9.29}$$

where:

$$F_i^{m,p,l} = f_i^{m,p,l} + \sum_{j=1}^{n} \alpha_{ij} \cdot y_j^{m,p,l} \tag{9.30}$$

Since no separation takes place, no separation efficiency has to be defined for mixing. The transformation of the particle size/liberation matrices $Ly_j^{m,p,l}$ and $Lf_i^{m,p,l}$ of the various input streams $\alpha_{ij} \cdot y_j^{m,p}$ and $f_i^{m,p}$ of the mixing operation to a new particle size/liberation matrix $Ly_i^{m,p,l}$ of the output of the mixer is defined by the following equation (Eq. 9.31).

$$\frac{f_i^{m,p} \cdot Lf_i^{m,p,l} + \sum_{j=1}^{n} \alpha_{ij} \cdot y_j^{m,p} \cdot Ly_j^{m,p,l}}{f_i^{m,p} + \sum_{j=1}^{n} \alpha_{ij} \cdot y_j^{m,p}}$$

$$= \frac{f_i^{m,p} \cdot Lf_i^{m,p,l} - \sum_{j=1}^{n} \alpha_{ij} \cdot y_j^{m,p} \cdot Ly_j^{m,p,l}}{F_i^{m,p}} = Ly_i^{m,p,l} \tag{9.31}$$

Formulation of model for metallurgical processing

The mass balance as well as the separation efficiency (recovery) of the metallurgical operations can be described in one equation (see Eq. 9.32). For the mass balance and separation efficiency for metallurgical processing the following equations (Eq. 9.32, Eq. 9.33 and Eq. 9.34) may be derived, representing respectively the mass balance and separation for stream y_i^k, x_i^k and z_i^k.

$$\sum_{p=1}^{p=5}\left(\left(\sum_{m=1}^{m=5}\left(\sum_{l=1}^{l=5} Lf_i^{m,p,l} \cdot C^{m,k,l}\right) \cdot f_i^{m,p}\right) \cdot Ry_i^{k,p}\right) - y_i^k = 0 \tag{9.32}$$

$$\sum_{p=1}^{p=5}\left(\left(\sum_{m=1}^{m=5}\left(\sum_{l=1}^{l=5} Lf_i^{m,p,l} \cdot C^{m,k,l}\right) \cdot f_i^{m,p}\right) \cdot Rx_i^{k,p}\right) - x_i^k = 0 \tag{9.33}$$

$$\sum_{p=1}^{p=5}\left(\left(\sum_{m=1}^{m=5}\left(\sum_{l=1}^{l=5} Lf_i^{m,p,l} \cdot C^{m,k,l}\right) \cdot f_i^{m,p}\right) \cdot Rz_i^{k,p}\right) - z_i^k = 0 \tag{9.34}$$

where:

$$Ry_i^{k,p} + Rx_i^{k,p} + Rz_i^{k,p} \tag{9.35}$$

Eq. 9.32, Eq. 9.33 and Eq. 9.34 calculate the fraction of each element k (Al wrought, Al cast, Steel, Cu and rest) present in each mineral class m of the input stream $f_i^{m,p,l}$ of metallurgical processing for the sum of all liberation classes based on the particle size/liberation matrix of the input $Lf_i^{m,p,l}$ and composition matrix $C^{m,k,l}$. The mass flows of the elements k (Al wrought, cast etc.) present in each mineral m are determined from the calculated fractions by multiplication the fractions with the mass flow of the input stream for each mineral m $f_i^{m,p}$. A transition from mineral m to element k is being made by adding up element k over all mineral classes m (mineral A becomes Al wrought, mineral B Al cast, etc.). The mass balance and separation efficiency over the metallurgical processing for each of these elements k is calculated based on the recovery values $Ry_i^{k,p}$, $Rx_i^{k,p}$ and $Rz_i^{k,p}$ as given in the model. Since in the output of metallurgical processes the definition of particle size classes make no sense, the recovered elements k are added up over all particle size classes or just simply alloy classes. the output y_k, x_k and z_k are only defined per element k. Therefore Eq. 9.32, Eq. 9.33 and Eq. 9.34 define the mass balance on element basis and not on mineral basis. The recovery values $Ry_i^{k,p}$, $Rx_i^{k,p}$ and $Rz_i^{k,p}$ can be a fixed value or can be dependent on the concentration of contaminants in the feed stream. The recovery value is then represented by (Eq. 9.36):

$$Ry_i^{k,p} - (a_p \cdot If_i^{k,p}) - b_p = 0 \tag{9.36}$$

where: $If_i^{k,p}$ is e.g. the organic content of the aluminium fraction being the input of the metallurgical process, and a_p and b_p are plant parameters (where b_p is equal to the recovery value for a certain size class p as given in the matrix) that define the variation of recovery as a function of $If_i^{k,p}$. The same applies to $Rx_i^{k,p}$ and $Rz_i^{k,p}$. The recovery values for metallurgical processing are only defined as being dependent on the particle size class, but not on the liberation class. The influence of liberation on the final metal recovery is taken into consideration by including the influence of the other elements, such as organics (= rest stream).

Alloy composition

The control and therefore the modelling of the alloy quality (composition) of the produced alloy are of utmost importance for the economic production of high quality metal products and the minimisation of waste production. The output composition of the metallurgical operation can be calculated by adding all elements present in the various material flows. The input to metallurgical processing (see Figure 9.4) is in the form of different size classes p, of which the composition is defined by combining the liberation/particle size matrix $Ly_i^{m,p,l}$ and the composition matrix $C^{m,l,k}$. The different aluminium alloys (wrought and cast), each with their own specific (average) composition is described by an alloy composition matrix in the model. The matrix defines the pure alloying elements for the defined aluminium alloys.

9.3.8 Parameterisation of the model

During product design, materials are chosen, and its combinations and connections among them are defined. These decisions will determine the mineralogy of the products and liberation attained by shredding, affecting the quality of intermediate recycling streams, the possibilities of material recovery and therefore the recycling rate of the product. Some connections between materials cannot be broken during shredding due to characteristics such as shape, size and strength of the connections, and ultimately due to the intrinsic randomness of the fracture paths originating from this comminution process [353]. This may result into the incomplete liberation of the materials connected. The two or more materials that remain attached in the non-liberated particles will end up in intermediate and product streams as dictated by the properties of the incompletely liberate particles after mechanical separation. These particles may therefore introduce foreign materials in the recovered stream that cannot be economically treated in the current thermal processing and/or pyrometallurgical systems as a function of thermodynamic limitations [33].

Data on liberation and particle size reduction during shredding

Data on the liberation of materials during shredding and data on the composition of the various liberation classes have never been measured up till now. Therefore estimations on this had to be made to set up the models. However the theoretical, model-based approach as presented in this and the previous chapter lays down a solid framework for data collection when setting up or performing recycling experiments. From various industrial experiments and shredder plants, which all involved a large number of car wrecks that were shredded and subsequently separated, data on both particle size reduction and liberation have been collected by sampling the various material flows within the shredder plants and analysing the composition, liberation distribution and the characteristics of the un-liberated particles. In Figure 9.6 to Figure 9.12 an impression is given from the appearance and material combinations encountered in the un-liberated particles/fractions. The different images given in Figure 9.6 to Figure 9.12 reveal

(a) (b)

Figure 9.6: (a) Hose clamp (steel) with rubber hose and copper; (b) Fragment of engine block - cast aluminium and steel

(a) (b)

Figure 9.7: (a) Drive shaft - steel and rubber; (b) Fragment of cylinder head - cast aluminium, steel and copper (valve guide)

immediately the influence of design, i.e. material combinations and types of connections, on the liberation and therefore on the maximum achievable quality of recycling (intermediate) products. Moreover Figure 9.6 to Figure 9.12 illustrate the complexity of describing the liberation and capturing the composition of the liberation classes in a model as discussed above.

The data as represented by the different images of Figure 9.6 to Figure 9.12 have been structured in order to function as a calibration for the developed models as discussed above as well as to be used as a basis for the further development and improvement of the models as developed up till now. These data are presented by Figure 9.13 to Figure 9.31. Due to the complexity of the data (see the diverse liberation properties in Figure 9.6 to Figure 9.12) it is difficult to define the composition matrix of liberation classes $C^{m,l,k}$ as discussed above, which captures all possible two- and multi-component material combinations in the un-liberated particles. Figure 9.13 gives the distribution of the liberated and un-liberated fraction over the four different particle size classes of the non-ferrous fraction after shredding, air suction and magnetic separation. Figure 9.14 presents the distribution of the "mineral" combinations in the un-liberated fraction for each particle size class as given in Figure 9.13, whereas Figure 9.15


(a) (b)

Figure 9.8: (a) Rubber with cable tree (copper and plastics); (b) Fragment of engine block - cast aluminium and steel bolts


(a) (b)

Figure 9.9: (a) Hose clamp (steel) on rubber hose; (b) 1 - Coils - copper and soft iron, 2 - Fragment of engine block - cast aluminium and steel bolts, 3 - Electronics - plastics and copper


(a) (b)

Figure 9.10: (a) Radiator - copper, brass, tin; (b) Radiator - copper, aluminium, plastics

(a) (b)

Figure 9.11: (a) Cylinder head - cast aluminium with steel insert; (b) 1 - Steering house - cast aluminium and steel, 2 - Cylinder head - cast aluminium and steel

(a) (b)

Figure 9.12: (a) Fragments of cylinder heads - cast aluminium and steel, valves - steel, and valve guide - copper; (b) Fragment of gear box housing - cast aluminium with steel bolts

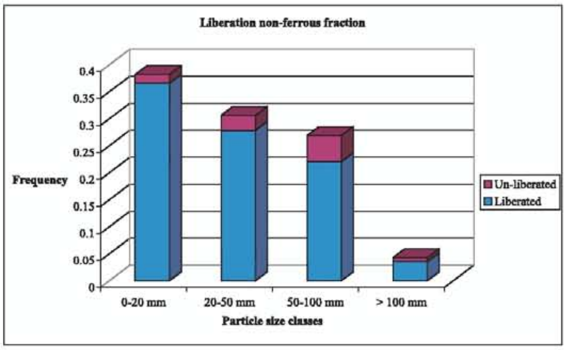


Figure 9.13: Distribution of liberated and non-liberated particles in the non-ferrous fraction for different particle size classes (after shredding, air suction and magnetic separation)

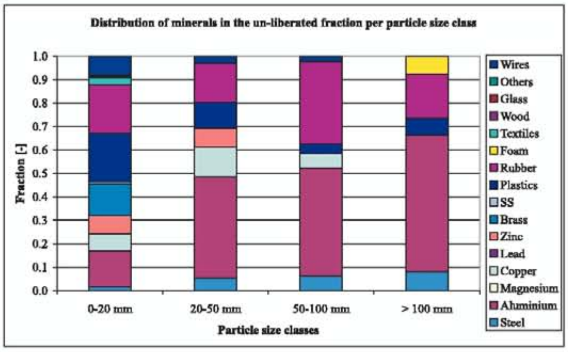
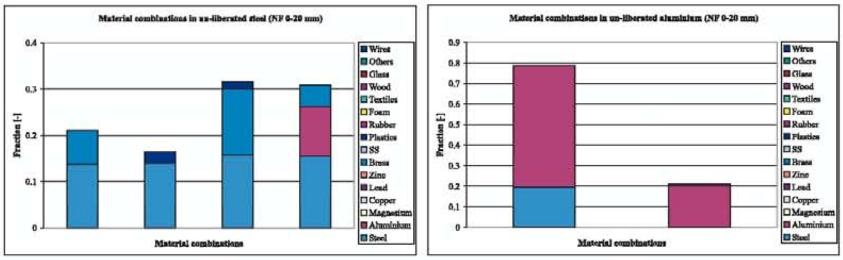


Figure 9.14: Distribution of the various minerals in the un-liberated fraction for each particle size class in the non-ferrous fraction (after shredding, air suction and magnetic separation)

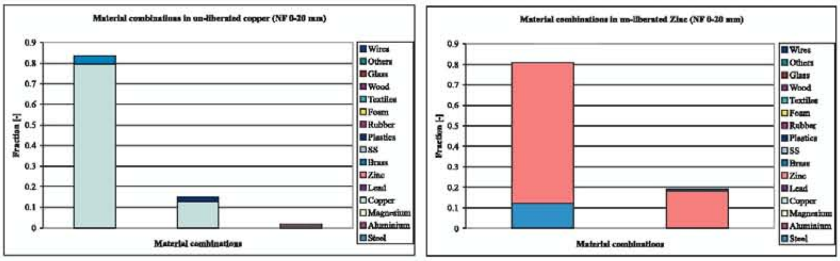
to Figure 9.31 illustrate for each mineral the various material combinations occurring in the un-liberated fraction for the different particle size fractions. The liberation data as represented in Figure 9.13 to Figure 9.31 is subject to a standard deviation on the measurements and analyses from the plant data, which is 0.3% for the mass flows and 5% for the analyses (material combinations in the un-liberated fractions).

Figure 9.32 [354] depicts the particle size/liberation matrix $L_{y_i}^{m,p,l}$ for the mineral aluminium in the NF fraction (see Figure 9.13). Figure 9.33 illustrates the composition matrix ($C^{m,l,k}$) representing the mass distribution of the different elements in the different liberation classes of aluminium in NF 20-50 mm (see Figure 9.32). Figure 9.34 depicts in detail the various material combinations in the un-liberated particles (liberation classes of Figure 9.33) for aluminium in NF 20-50 mm. For each particle type, in each liberation class, the mass percentage of the different elements composing the particle is represented. Different connection types have been defined in order to predict the breakage and liberation during shredding as a function of design choices on materials associations and the type of connection (see Figure 9.35).



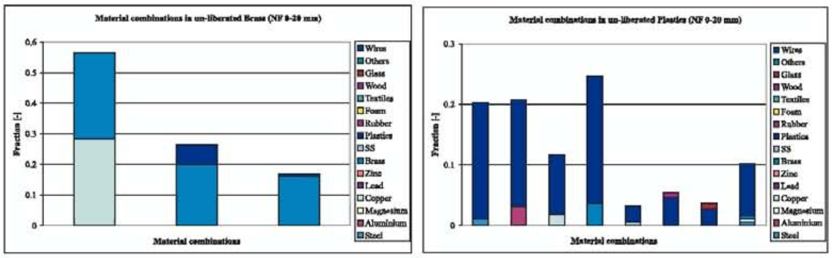
(a) (b)

Figure 9.15: Material combinations in (a) un-liberated steel; (b) un-liberated Al - NF fraction 0-20 mm



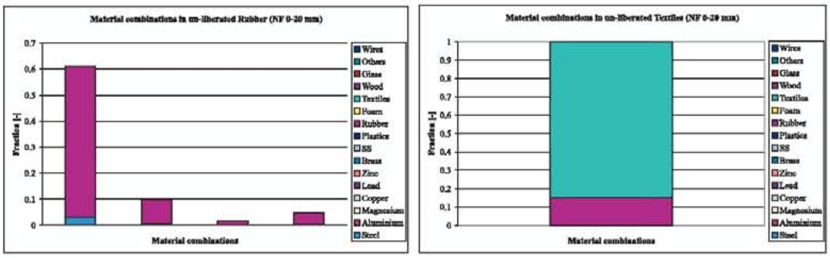
(a) (b)

Figure 9.16: Material combinations in (a) un-liberated copper; (b) un-liberated zinc - NF fraction 0-20 mm



(a) (b)

Figure 9.17: Material combinations in (a) un-liberated brass; (b) un-liberated plastics - NF fraction 0-20 mm



(a) (b)

Figure 9.18: Material combinations in (a) un-liberated rubber; (b) un-liberated textiles - NF fraction 0-20 mm

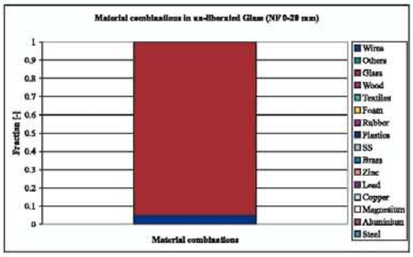
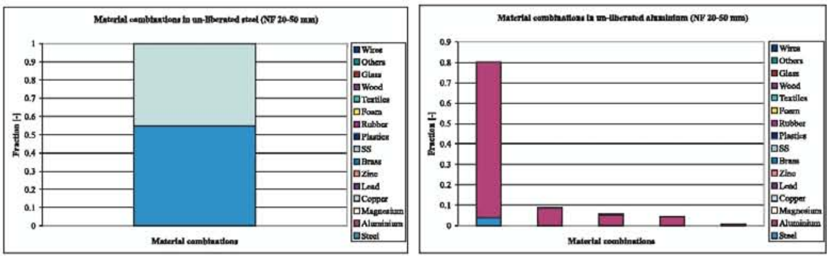
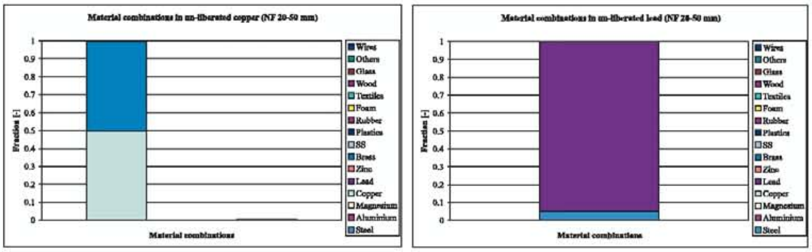


Figure 9.19: Material combinations in un-liberated glass - NF fraction 0-20 mm



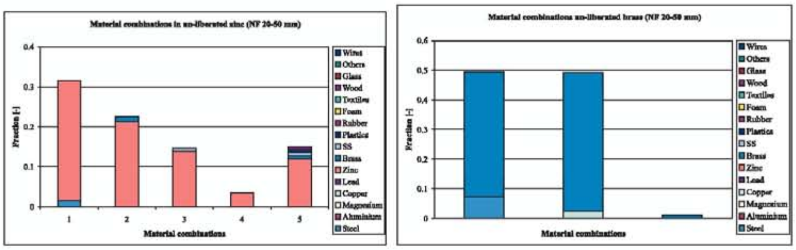
(a) (b)

Figure 9.20: Material combinations in (a) un-liberated steel; (b) un-liberated Al - NF fraction 20-50 mm



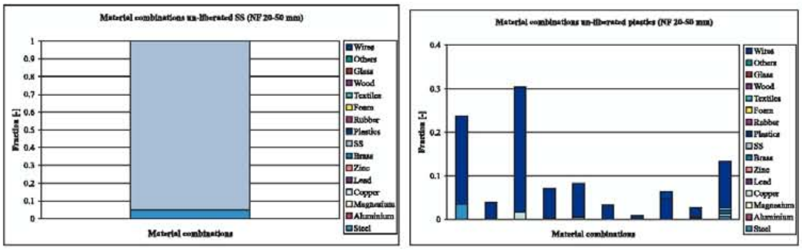
(a) (b)

Figure 9.21: Material combinations in (a) un-liberated copper; (b) un-liberated lead - NF fraction 20-50 mm



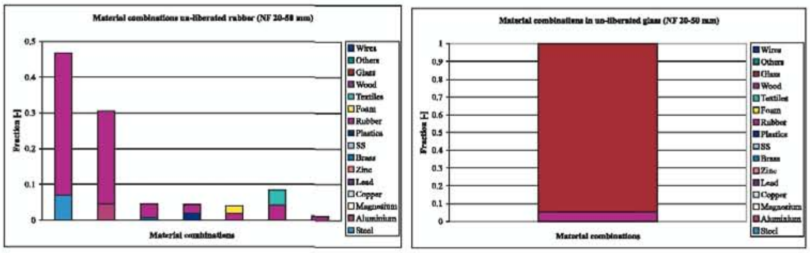
(a) (b)

Figure 9.22: Material combinations in (a) un-liberated zinc; (b) un-liberated brass - NF fraction 20-50 mm



(a) (b)

Figure 9.23: Material combinations in (a) un-liberated SS; (b) un-liberated plastics - NF fraction 20-50 mm



(a) (b)

Figure 9.24: Material combinations in (a) un-liberated rubber; (b) un-liberated glass - NF fraction 20-50 mm

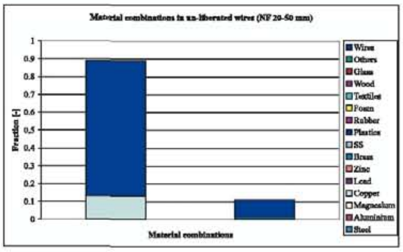
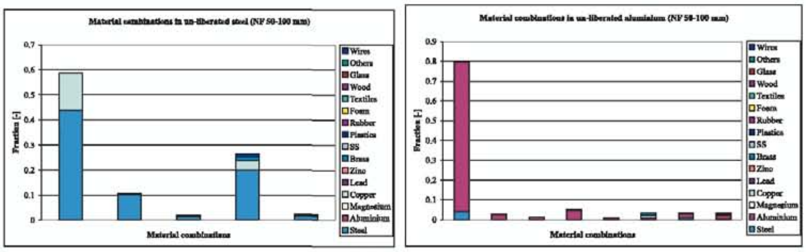
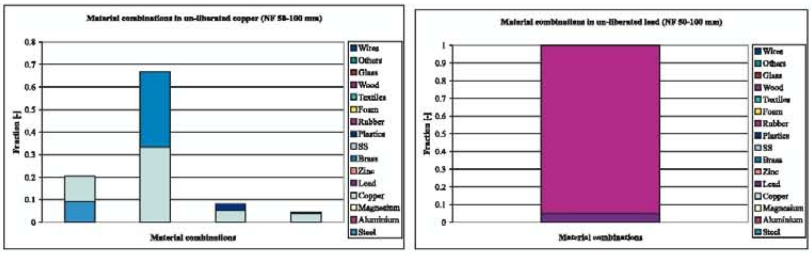


Figure 9.25: Material combinations in un-liberated wires NF fraction 20-50 mm



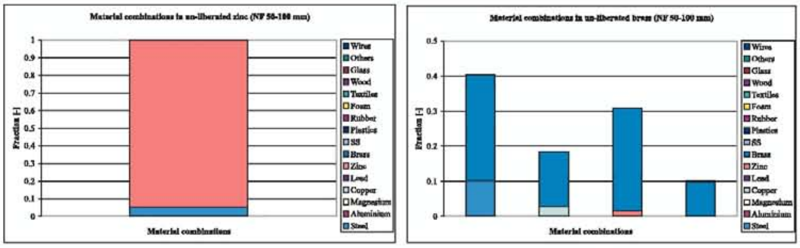
(a) (b)

Figure 9.26: Material combinations in (a) un-liberated steel; (b) un-liberated Al - NF fraction 50-100 mm



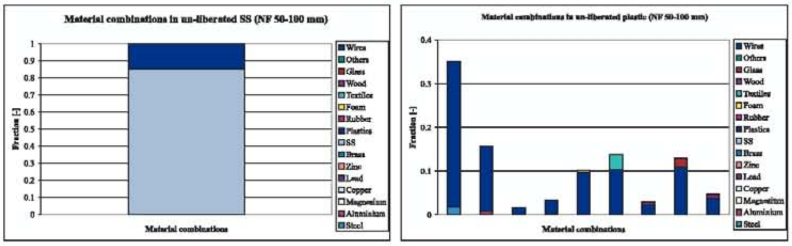
(a) (b)

Figure 9.27: Material combinations in (a) un-liberated copper; (b) un-liberated lead - NF fraction 50-100 mm



(a) (b)

Figure 9.28: Material combinations in (a) un-liberated zinc; (b) un-liberated brass - NF fraction 50-100 mm



(a) (b)

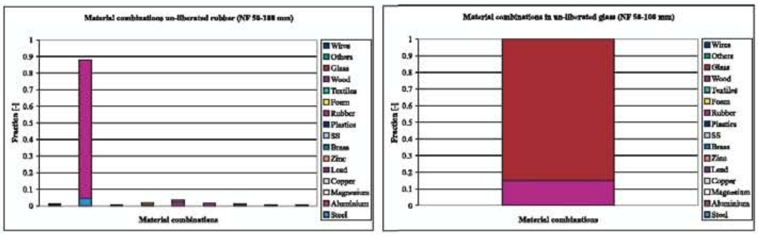
Figure 9.29: Material combinations in (a) un-liberated SS; (b) un-liberated plastics - NF fraction 50-100 mm

9.3.9 Linking design to recycling

Figure 9.13 to Figure 9.31 illustrate the wide range of material combinations present in unliberated materials as a function of the various particle size fractions after shredding. This reveals that the composition matrix $C^{m,l,k}$ of the liberation classes for each mineral A to E (steel, aluminium, copper, etc.) as defined above do not give the possibility to describe each random combination of materials within the different liberation classes as present after shredding (see Figure 9.13 to Figure 9.31). However, this definition provides a first and crucial step to incorporate design, particle size reduction and liberation in the description and optimisation of recycling systems. The recycling models as developed provide a first principles basis to link design and recycling as is required by the automotive industry at this moment. The developed models provide the basis to further develop this theory; collect and incorporate data as e.g. given in Figure 9.13 to Figure 9.31, which is essential to improve the description of liberation. This is required in order to link particle size reduction and liberation with the joints and material combinations as defined in the CAD of product design. The recycling optimisation models define the effect of liberation and material combinations on the recycling system. In order to make it possible to ultimately link design to recycling, knowledge from the recycling system (as provided by the models as well as by the data of Figure 9.13 to Figure 9.31) should be applied to define car design (being the input of the shredder), in view of material combinations and connections. In order to realise this, the description of the composition matrix $C^{m,l,k}$ and therefore liberation classes has to be improved. A basis for this is provided by the data of Figure 9.13 to Figure 9.31, however more detailed information on individual particle composition should be collected in addition to the data provided by Figure 9.13 to Figure 9.31. Furthermore, the transformation of particle size and liberation over the shredder has to be modelled; more research and data collection are required to realise this. This must be done in close relation to a proper definition of the car in view of recycling in order to link design properties (material combinations, material connections, type of connections, size of connections, etc.) to the definition of particle size and liberation after shredding. This could be done using the first principles basis of the recycling optimisation model as developed in this thesis work.

Castro et al. (2004b)[176] have developed a design simulation tool, which connects product characteristics (composition and material connections) defined during the design phase with liberation of these materials during shredding as a function of joint types. The model shows how design choices affect the feed to recycling systems by the application of a hierarchical decision tree model, which should be combined with the recycling models as described here. The combination of these models could establish a future bridge between the knowledge areas of product design and recycling, hence providing a tool which the designer can use in the process of car design. These models could be used as a basis to translate the detailed knowledge of liberation and recycling to the language and tools of product designers in future. Note that the link between design software and recycling models has not been established yet, although the recycling optimisation models give a clear indication how this link should be realised by using the data as provided in Figure 9.13 to Figure 9.31.

By studying the modelling principles of minerals processing systems, a direction could be found to define the design of the car in relation to recycling, which is essential to apply design for recycling. However, the fundamental differences as well as the analogies of comminution modelling in minerals processing and shredding modelling in recycling of cars need further investigation to finally link design and recycling on a proper fundamental basis.



(a) (b)

Figure 9.30: Material combinations in (a) un-liberated rubber; (b) un-liberated glass - NF fraction 50-100 mm

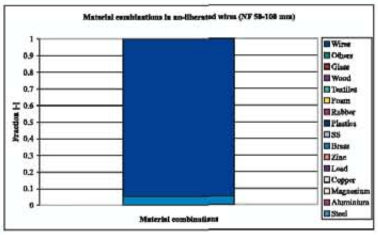


Figure 9.31: Material combinations in un-liberated wires - NF fraction 50-100 mm

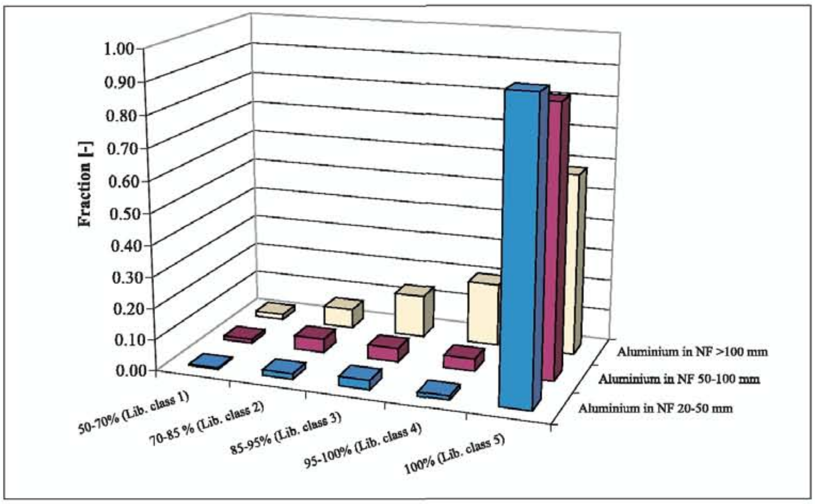


Figure 9.32: Particle size/liberation matrix $L_{y_i}^{m,p,l}$ for aluminium

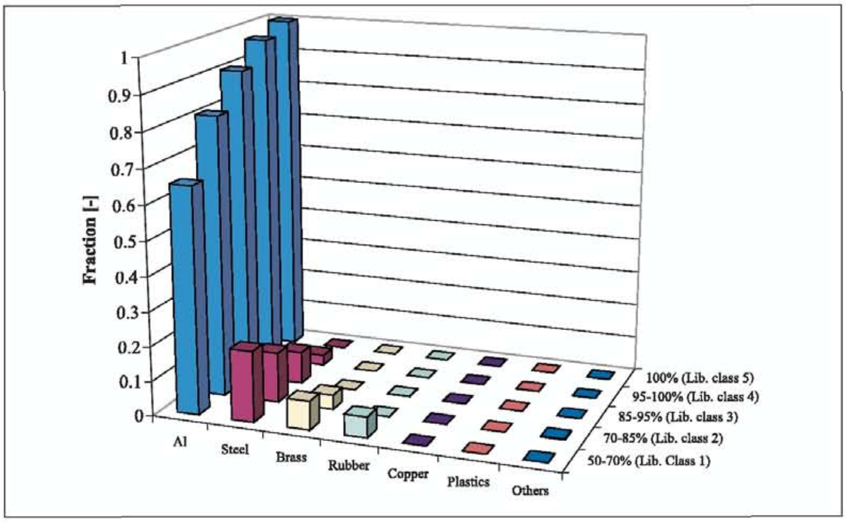


Figure 9.33: Composition matrix for aluminium in NF 20-50 mm

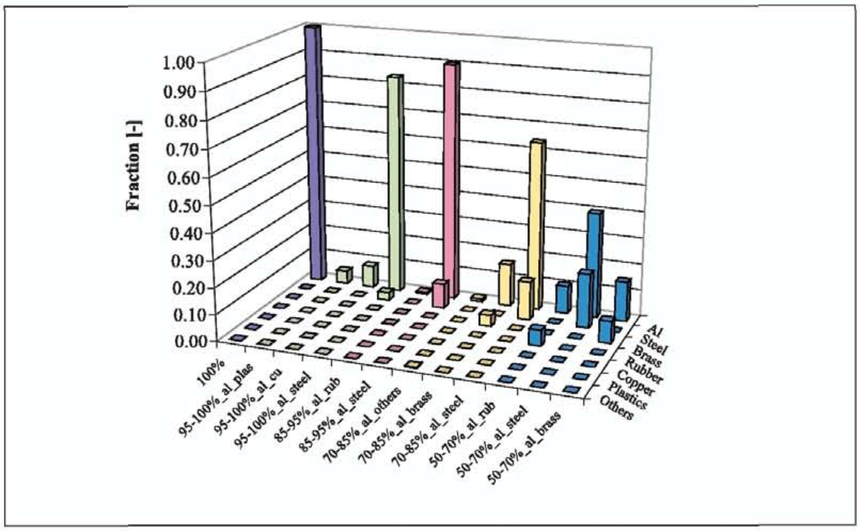


Figure 9.34: Description of particle types showing the compositions of the different unliberated particles for the mineral aluminium (see Figure 9.33) within the different liberation classes in NF 20-50 mm

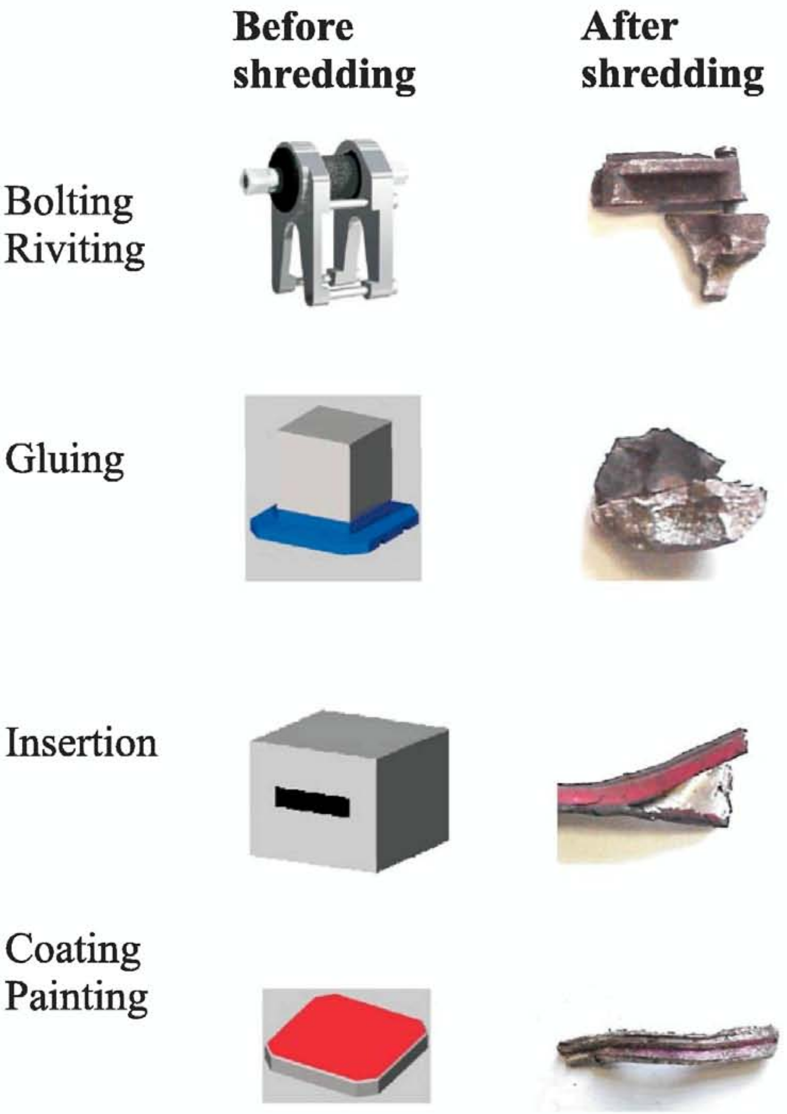


Figure 9.35: Joint types depicted before and after shredding - Examples of connections defined based on industrial data of shredded particles

9.3.10 Simulations on the optimization of product design, liberation and metallurgy

The developed recycling optimization model was used for four different case studies. The results of these simulations are discussed showing the relationship between the in- and output of the shredder. These simulations will reveal that the breakage behaviour for modern consumer products differs fundamentally from traditional minerals processing. Moreover the four different simulation scenarios are applied to calculate the effect of changes in product design and hence particle size reduction and liberation on the recycling of end-of-life vehicles. Therefore also the relationship to recycling rate is discussed. The recycling optimization model is depicted in Appendix C.3.

Software for optimization

The software application used to perform the modelling of the shredder as well as the optimization of the recycling flowsheet as depicted in Figure 9.4 is Frontline Systems'®Premium Solver Platform, extended with the Large-Scale GRG Non-linear Solver [328], implemented in Microsoft®Excel [327]. This solver platform is capable of handling these large scale, complex, non-linear optimization problems (see Appendix C.3).

Simulation of the shredder

Scenarios Since data on the relation between particle size reduction and liberation during shredding of end-of-life products is lacking, no model for the transformation of the particle size and liberation distributions during shredding could be developed. However, the relation between the in- and output of the shredding operation is investigated by calculating the liberation distribution of the output of a shredding step, therefore estimating the liberation matrix (Eq. 9.13), based on a fixed particle size reduction (Eq. 9.11 and 9.12) (by defining a shredding matrix Sf_i^{m,p_f,p_y} for the transformation of the particle size distribution) for different input definitions $f_i^{m,p,l}$ (mass based particle size distribution) and $Lf_i^{m,p,l}$ (liberation distributions) of the shredding step (which are representing differences in product design). The relation between the liberation distribution of the input ($Lf_i^{m,p,l}$) and the output ($Ly_i^{m,p,l}$) is calculated based on the optimization of the closure of the mass balances for all elements (Eq. 9.13) over the shredding process, for different starting values for the input distributions defined for the four different scenarios. This relationship illustrated the complexity of the breakage matrix for liberation. The optimization and calculations are performed using Microsoft® Excel [327]. As can be seen from Table 9.8 (a) to (d) the liberation distributions of the output are defined as a diagonal matrices in these simulations. However, this does not have to be the case in practice, but is done here for reasons of clarity.

Simulations Scenarios 1 and 2 illustrate the effect of the liberation distribution of the input. The input distribution of the liberation for scenario 1 is shifted to the lower liberation classes (no or poorly liberated materials in the design of the car), whereas simulation 2 calculates the liberation distribution of the output based on an liberation distribution of the input shifted to the higher liberation classes (more/better liberated materials in the design of the car). The particle size distribution of the input is defined for both simulations in class 1 (largest particle size class). The influence of the particle size distribution of the product design (input) on the shredding operation is illustrated by simulations 3 and 4. The definition of the liberation distribution of the input of simulation 3 is shifted to the lower liberation classes (similar to simulation 1), whereas the input of simulation 4 is shifted to the higher classes (similar to

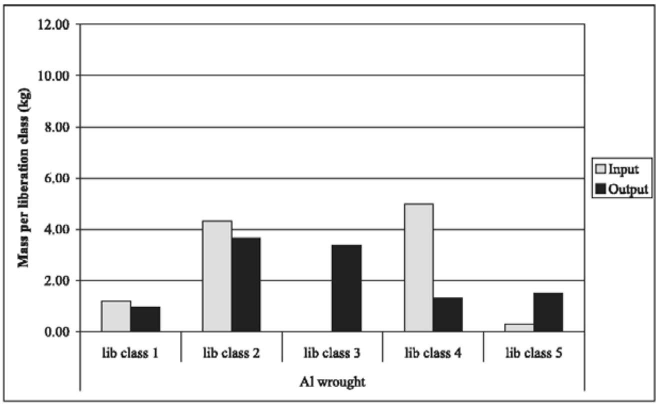


Figure 9.36: Mass (kg) of element Al wrought in mineral A for liberation classes 1 to 5 over all particle size classes p for the input and output of the shredding operation for scenario 1

simulation 2) (see Table 9.8(a) to (d)). The simulation results of the four different scenarios for mineral A are depicted by Table 9.8(a) to (d). For each of the other minerals (B to E) the same simulations have been performed. The results clearly illustrate the relationship between the input definition (particle size and liberation distribution) on the liberation distribution of the output of the shredder, with each input definition resulting in a different shredder output for liberation of the materials.

Discussion Figure 9.36 to Figure 9.39 depict the mass of the different elements k (shown for Al wrought and Fe) in the liberation classes 1 to 5 over all particle size classes p for the input and output of the shredding operation for mineral A for simulation scenario 1 and 2. For the other elements k and minerals m similar figures can be drawn for all simulation scenarios performed. Figure 9.36 to Figure 9.39 reveal that the definition of particle size distribution combined with the liberation distribution of the input (car design) determine the amount (kg) of the different elements k in the in- and output of the shredding process, as well as the final amount (kg) of liberated/non-liberated materials/elements after shredding. Two different conclusions on the liberation behaviour of modern consumer products can be drawn from the simulations performed based on Figure 9.36 to Figure 9.39.

- During shredding, the major element composing the defined mineral (e.g. Al wrought for mineral A) will liberate. However, the other elements in this mineral can become less liberated, due to the definition of the composition of liberation classes as discussed above. When the major element of a defined mineral liberates from the other elements, the remaining elements in a particle could be present in a less liberated class (a lower fraction of the major element combined with higher fractions of the others).
- Moreover, shredding of modern consumer goods not necessarily leads to an increased amount of mass in all higher liberation classes of the output compared to the input distribution for the major element composing a defined mineral. This in contradiction to the liberation of mineral ores.

Table 9.8: (a) to (d) Particle size class distribution (kg) and liberation class distribution (-) of mineral A for the input and output of the shredder operation for respectively (a) scenario 1; (b) scenario 2; (c) scenario 3 and; (d) scenario 4

	Part. size class	Total mass	lib. class 1	lib. class 2	lib. class 3	lib. class 4	lib. class 5
INPUT	(a) Scenario 1						
A in ELV	1	15.000	0.158	0.442	0.000	0.381	0.020
A in ELV	2	0.000	1.000	0.000	0.000	0.000	0.000
A in ELV	3	0.000	1.000	0.000	0.000	0.000	0.000
A in ELV	4	0.000	1.000	0.000	0.000	0.000	0.000
A in ELV	5	0.000	1.000	0.000	0.000	0.000	0.000
OUTPUT							
A in shredded	1	3.000	0.632	0.367	0.000	0.000	0.000
A in shredded	2	4.500	0.000	0.999	0.000	0.000	0.000
A in shredded	3	4.500	0.000	0.000	1.001	0.000	0.000
A in shredded	4	1.500	0.000	0.000	0.000	0.999	0.000
A in shredded	5	1.500	0.000	0.000	0.000	0.000	0.999
INPUT	(b) Scenario 2						
A in ELV	2	0.000	0.000	0.000	0.000	0.000	0.000
A in ELV	3	0.000	0.000	0.000	0.000	0.000	0.000
A in ELV	4	0.000	0.000	0.000	0.000	0.000	0.000
A in ELV	5	0.000	0.000	0.000	0.000	0.000	0.000
OUTPUT							
A in shredded	1	3.000	0.255	0.129	0.240	0.184	0.190
A in shredded	2	4.500	0.000	0.165	0.313	0.286	0.236
A in shredded	3	4.500	0.000	0.000	0.461	0.286	0.252
A in shredded	4	1.500	0.000	0.000	0.000	0.560	0.441
A in shredded	5	1.500	0.000	0.000	0.000	0.000	0.999
INPUT	(c) Scenario 3						
A in ELV	2	5.000	0.000	0.623	0.078	0.239	0.060
A in ELV	3	5.000	0.153	0.427	0.000	0.421	0.000
A in ELV	4	0.000	0.000	0.000	0.000	0.000	0.000
A in ELV	5	0.000	0.000	0.000	0.000	0.000	0.000
OUTPUT							
A in shredded	1	1.000	0.000	0.999	0.000	0.000	0.000
A in shredded	2	4.000	0.000	0.999	0.000	0.000	0.000
A in shredded	3	5.500	0.000	0.000	0.999	0.000	0.000
A in shredded	4	2.500	0.000	0.000	0.000	0.999	0.000
A in shredded	5	2.000	0.000	0.000	0.000	0.000	0.999
INPUT	(d) Scenario 4						
A in ELV	1	5.000	0.114	0.019	0.000	0.868	0.000
A in ELV	2	5.000	0.003	0.104	0.000	0.894	0.000
A in ELV	3	5.000	0.018	0.000	0.000	0.756	0.227
A in ELV	4	0.000	0.000	0.000	0.000	0.000	1.000
A in ELV	5	0.000	0.000	0.000	0.000	0.000	1.000
OUTPUT							
A in shredded	1	1.000	0.238	0.202	0.185	0.203	0.171
A in shredded	2	4.000	0.000	0.042	0.223	0.521	0.213
A in shredded	3	5.500	0.000	0.000	0.412	0.452	0.135
A in shredded	4	2.500	0.000	0.000	0.000	0.995	0.004
A in shredded	5	2.000	0.000	0.000	0.000	0.000	0.999

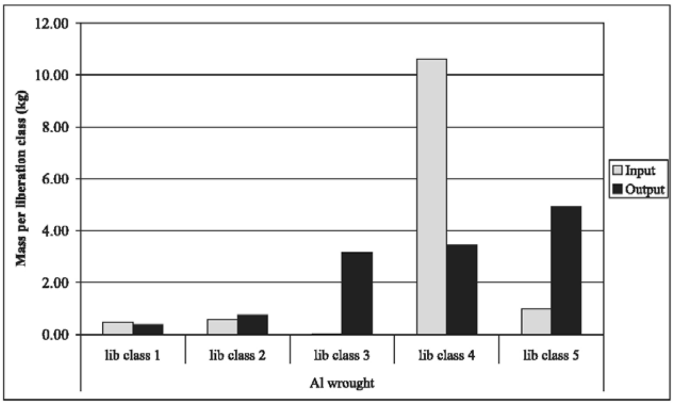


Figure 9.37: Mass (kg) of element Al wrought in mineral A for liberation classes 1 to 5 over all particle size classes p for the input and output of the shredding operation for scenario 2

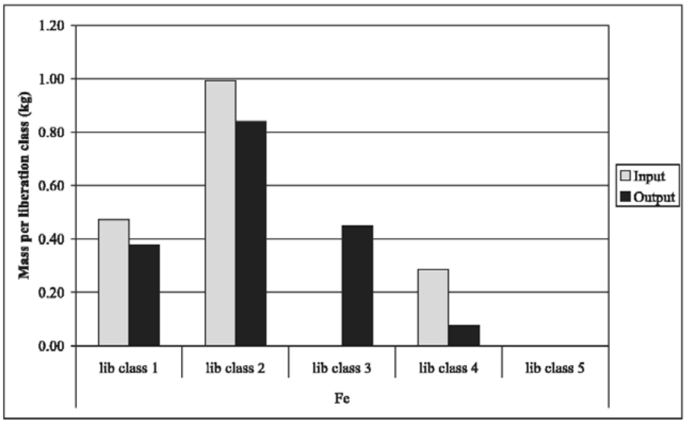


Figure 9.38: Mass (kg) of element Fe wrought in mineral A for liberation classes 1 to 5 over all particle size classes p for the input and output of the shredding operation for scenario 1

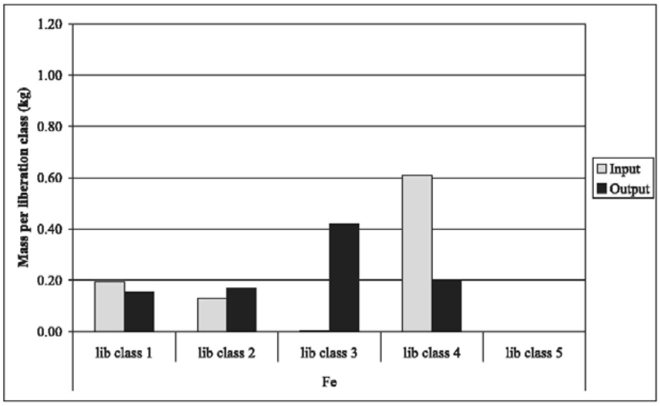


Figure 9.39: Mass (kg) of element Fe in mineral A for liberation classes 1 to 5 over all particle size classes p for the input and output of the shredding operation for scenario 2

As can be seen from Figure 9.36 to Figure 9.39 the mass of the major element in the mineral in the lowest liberation class (class 1) will decrease due to shredding, whereas the mass of materials in the higher liberation class(es) increases. The mass in the intermediate liberation classes not necessarily increases, due to the same liberation behaviour as described for the liberation of the other elements. This suggests a fundamental difference between the liberation behaviour of mineral ores and man-made minerals (consumer goods). Simulations on the optimization the recovery/recycling rate as a function of design, shredding and recycling processes The influence of product design, shredding, particle size reduction and liberation on the efficiency of mechanical separation, the quality of intermediate recycling streams and final metallurgical recovery is discussed based on the four defined scenarios. The final metal recovery is calculated using the developed recycling optimization model for recycling end-of-life vehicles, including the processes and material flows as depicted in Figure 9.4. Table 9.9 gives the simulation results using the recycling optimization model for the four different scenarios as defined above. Table 9.9 reveals the effect of a changing input (particle size of input in combination with the liberation) on the final metal recovery as well as on the total recycling rate of the car. It becomes clear from the simulation results how a better design (less material connections in the design) contributes to the optimization and realisation of recycling targets as imposed by legislation. It must be noted that the recovery and recycling rates as calculated here do not intend to represent real values, but are used to illustrate the influence of changing design and shredding performance. The recovery of the non-metal content of the car is defined to be 0%, which is not necessarily the case. The results also reveal the importance of describing recycling systems based on particle size and liberation properties of the materials involved.

Table 9.10 shows the composition of the produced aluminium alloy for the different scenarios to reveal the effect of design and shredding (particle size and liberation) on the final material quality based on the defined scenarios using the recycling optimization model. The model has not taken into account the quality requirements imposed on the input of e.g. metallurgical processes. However, Table 9.10 reveals that the liberation and particle size influence the quality of intermediate recycling streams produced by mechanical separation as well as the final metal quality. Poorly liberated material could lead to unacceptable contaminations

Table 9.9: Recovery rate for the metal content and recycling rate of passenger vehicles calculated from the recycling optimization model for the different scenarios (%)

	Recovery rate metals(%)	Recycling rate car (%)
Scenario 1	78.5	58.6
Scenario 2	80.1	59.8
Scenario 3	78.6	58.5
Scenario 4	82.8	62.8

of the produced recycling streams, which are the feed to metallurgical processes.

Table 9.10: Composition of produced aluminium alloy for the different scenarios given for the fraction of Al, Si, Fe and Cu

	Al	Si	Fe	Cu	Others
Scenario 1	0.60	0.06	0.21	0.12	0.01
Scenario 2	0.69	0.07	0.14	0.08	0.01
Scenario 3	0.67	0.07	0.17	0.09	0.01
Scenario 4	0.66	0.07	0.16	0.10	0.01

9.4 Discussion

Product design not only influences the use phase of the product, but also has a significant influence on the recycling due to its 'mineralogy' or design. The material connections and combinations in the design of the car determine the particle size reduction and the degree of liberation of the product during shredding, which affects the composition of the intermediate recycling streams (composition and amount of the non-liberated particles) and the efficiency of physical separation. The quality of intermediate recycling products is of critical importance in order to optimise the material recovery in metallurgical processing, which is the closer of the material cycle.

- Two different recycling optimization models have been developed, in which (1) the liberation of the materials and (2) both the particle size reduction as well as the liberation of the materials were included as modelling parameters. The modelling and definition of the particle size reduction and liberation is developed based on the knowledge available from the modelling of minerals processing systems.

- The modelling and optimization of the recycling of end-of-life consumer products such as passenger vehicles is closely related to the modelling and simulation of traditional minerals processing systems. It is illustrated in this chapter how the knowledge of traditional fields such as mineral processing technology can be applied in the field of (design for) recycling of complex consumer goods.

- The modelling of liberation (and particle size reduction) is crucial to lay down a fundamental basis, which makes it possible to link in future design with final metal and material recovery, therefore, recycling rate.

- The modelling of liberation is necessary in order to optimise the resource cycle as well as to describe the quality of the products, not only due to imperfect separation, but also due to incomplete liberation of the different minerals composing the car. Liberation during shredding is the link between design and recycling.
- In order to apply a systematic approach to desired and problematic material combinations in product design and intermediate recycling products, a material matrix has been developed depicting the consequences of material combinations in intermediate recycling products (achieved by product design, liberation and mechanical separation) on metallurgical process efficiency (losses or contamination of end product). Based on this matrix it becomes clear which material combinations have to be liberated during shredding, separated during mechanical recycling, or should be avoided in product design.
- The effect of the product mineralogy, liberation on the quality of intermediate recycling products and as a consequence on the recovery of materials and the quality of the output becomes clear from simulations using the developed recycling optimization model for recycling end-of-life vehicles. From this the following could be concluded:
    - Modern society minerals are complex, so divers and changing so rapidly making a fundamental description very difficult, since data collection on the relationship between particle size and liberation during shredding has not been considered up till now. However the simulations reveal the complexity of modelling the breakage matrix for shredding modern consumer goods;
    - The liberation behaviour of modern consumer products differs fundamentally from that of mineral ores. This implies that what is true for classical grinding i.e. the finer the grind the more liberated particles become is not necessarily true for shredding of end-of-life consumer goods;
    - The modelling of multi-component systems for liberation reveals the fact that during shredding, the major element composing a mineral will liberate. However, the other elements in this mineral could become less liberated;

      The design of a product and the related particle size reduction and liberation efficiency during shredding are of critical importance in achieving a **high quality** feed to metal producing processes to ensure high **recycling rates**;
    - Optimization of the resource cycle of passenger vehicles can never be realised without proper understanding of the effect of design, liberation and particle size reduction on the closing of the material cycle, something that is well understood in the processing of mineral ores.
- Since data on the liberation of materials during shredding and data on the composition of the various liberation classes have never been measured up till now, estimations on this had to be made to set up the models. Recycling systems have never really been analysed systematically as classical minerals processing has done in the past.
- This chapter discusses the significant influence of product mineralogy, expressed in material combination as well as construction, and the liberation during shredding on the final material recovery and product quality in recycling modern consumer products, such as passenger vehicles. Optimization of the resource cycle of passenger vehicles can never be realised without proper understanding of the effect of these parameters on the closing of the material cycle.

- In summary it can be stated that the knowledge built up over many years within the field of minerals processing can contribute significantly to improving the transparency, quality and control of recycling systems and design for recycling and metal recovery. Moreover it should be realised that the future of minerals processing technology could lie in the growing field of recycling consumer products, which are becoming the new mineral ores of the next decades.

Nomenclature

a_p, b_p	Parameters in grade-recovery relationships for a particle size class p
α_{ij}	Structural parameters linking unit operation j with i
$C^{m,l,k}$	Composition matrix, defines for each mineral m the composition of the different liberation classes l for the elements k
$f_i^{m,l}$	Feed of mineral m in liberation class l for unit operation i (kg)
$F_i^{m,l}$	Sum of feed of mineral m in liberation class l for unit operation i (kg)
$f_i^{m,p,l}$	Feed of mineral m in particle size class p and liberation class l for unit operation i (kg)
$F_i^{m,p,l}$	Sum of feed of mineral m in particle size class p and liberation class l for unit operation i (kg)
i, j	Plants, unit operations, transport, etc., with $1 \rightarrow n$ representing the total amount of units (dismantling, shredding, magnetic separation, non-ferrous separation, metallurgical unit operations, etc.)
$If_i^{k,p}$	Organic content of metal fraction f_i for element k in particle size class p
k	Elements, metals, compounds originating from the different material streams in the recycling flow sheet of end-of-life vehicles (Al wrought, Al cast, steel, copper, other materials such as other non-ferrous metals, organic materials, glass, etc.)
l	Liberation classes with $l = 1 \rightarrow 5$
$Lx_i^{m,p,l}$	Liberation/particle size matrix, defines for each mineral m the liberation classes l present in the different particle size classes p for the material stream x_i after each unit operation i
$Ly_i^{m,p,l}$	Liberation/particle size matrix, defines for each mineral m the liberation classes l present in the different particle size classes p for the material stream y_i after each unit operation i
$Lz_i^{m,p,l}$	Liberation/particle size matrix, defines for each mineral m the liberation classes l present in the different particle size classes p for the material stream z_i after each unit operation i
m	Minerals A (Al wrought based), B (Al cast based), C (Rest based), D (Steel based), E (copper based)
p	Particle size classes with $p = 1 \rightarrow 5$
$Rx_i^{k,p}$	Recovery for metallurgical processing of element k in particle size class p to stream x for unit operation i
$Ry_i^{k,p}$	Recovery for metallurgical processing of element k in particle size class p to stream y for unit operation i
$Rz_i^{k,p}$	Recovery for metallurgical processing of element k in particle size class p to stream z for unit operation i
Sf_i^{m,p_F,p_y}	Shredding matrix for the transformation of the particle size distribution for mineral m
$Sf_i^{m,l}$	Shredding matrix for the transformation of the liberation distribution for mineral m
$Sy_i^{m,l}$	Liberation matrix, defines for each mineral m the liberation

	classes l present for the material stream y_i after each unit operation i
$Tx_i^{m,p,l}$	Transformation matrix for mechanical separation processes i defining the recovery for each mineral m for each particle size class p and liberation class l to stream x_i
$Ty_i^{m,p,l}$	Transformation matrix for mechanical separation processes i defining the recovery for each mineral m for each particle size class p and liberation class l to stream y_i
$Tz_i^{m,p,l}$	Transformation matrix for mechanical separation processes i defining the recovery for each mineral m for each particle size class p and liberation class l to stream z_i
$x_i^{m,p,l}$	Flow rate of mineral m in particle size class p and liberation class l to stream x of unit operation i (kg)
$y_i^{m,p,l}$	Flow rate of mineral m in particle size class p and liberation class l to stream y of unit operation i (kg)
$z_i^{m,p,l}$	Flow rate of mineral m in particle size class p and liberation class l to stream z of unit operation i (kg)

Chapter 10

Recycling experiments - from theory to practice

It is essential for the practical use and reliability of the optimization and dynamic model that useful data should be available, all within the statistical limits of sampling and mass balancing. Up to now, due to poor theoretical understanding of recycling systems, these data are not available and have not been collected in a proper manner. Furthermore, the lack of these data within a statistical framework makes any meaningful calculation of recycling rate impossible or in fact the ISO norm is practically of no use and legal consequence, in short, it is flawed! The developed theory as described in the previous chapters provides a fundamental basis for proper collection of data, supported by a good mass balance based on data reconciliation, and the corresponding statistics and how this should be performed when carrying out experiments or auditing a plant. This theory is essential to characterise and control the material and element flows in recycling plants, which is extremely important for good metal/material accounting, the calculations of recycling rate on a sound statistical basis, as well as quality control of recycling streams. Experimental and industrial data on the composition of the car, the separation efficiency of the various processes, liberation and particle size reduction in the shredder, the quality (or grade) of the recycling (intermediate) material streams is typical information that becomes available through a good understanding of the theory of recycling. Furthermore, the collection of industrial data on recycling based on best available technology is essential to predict and calculate the recyclability of passenger vehicles, using the developed models. This is of extreme importance for the type approval of vehicles. In this chapter a methodology is presented how recycling rates should be determined in practice based on this sound fundamental basis, which is a basis for a modified ISO norm. Subsequently a procedural basis is provided from which the recycling rate can be calculated from an industrial experiment, in which 1153 end-of-life vehicles were recycled. This experiment was initiated and managed by Auto Recycling Nederland BV, executed at CometSambre in Belgium and for which the procedure was laid down; the analyses were carried out; and mass balance and recycling rate calculations were performed at Delft. Therefore this chapter demonstrates how recycling rates can (should) be calculated from data collected from recycling experiments, referring to the various methodologies to be used in such experiments, based on the developed theory.

10.1 Introduction

It is surprising how poorly mass balances are performed in industry and how poorly data statistics (i.e. average and standard deviation) are understood and respected. Large and expensive shredding campaigns are performed but one can at most consider the reported results with contempt due to the poor understanding of sampling theory and statistics reflected in these reports. In Chapters 7 through 9 the fundamental theory has been laid down, which describes both the statistically distributed and dynamic nature of the resource cycle as well as the knowledge required to describe, understand and optimise recycling systems on a technological basis. This theory has been developed based on the theory available from classical minerals processing, systems engineering and process control combined with practical knowledge of recycling systems. The calculation and prediction of recycling rates using the developed models as well as linking design models to recycling software requires the availability of sound industrial data, collected based on a fundamental understanding of recycling, within a statistical framework, representing the distributed reality of car design, statistics around measurements on industrial plants, as well as the statistical behaviour of the performance of separation processes, the quality of recycling (intermediate) products and plant practice. The results derived from recycling tests, which have been performed up till now by various institutes and companies (e.g. Franois, [355]; Ansems et al. [330]) in order to determine e.g. the recyclability of a product or to function as the basis of design for recycling tools, are debatable due to the lack of fundamental knowledge of recycling systems, placed in the framework of system dynamics and statistics. The small size of the products processed and the lack of a sound statistical and sampling basis for the calculation of results, based on a mass balance which cannot be closed for both the total mass flow as well as the mass flow of the components composing the product, renders these debatable. Moreover, the relation between product design, liberation in the shredder and the recycling rate of products was first discussed by Van Schaik et al. [6] and has till that moment not been part of recycling tests and design for recycling tools.

The theory and models as discussed in the previous chapters provides a fundamental basis for proper collection of data [6, 356, 51]. The data collection have to be supported by a good mass balance, which can be derived using the technique of data reconciliation, and the corresponding statistics and how this should be performed when carrying out experiments or auditing a plant. This theory is essential to characterise and control the material and element flows in recycling plants, which is extremely important for good metal/material accounting, the calculations of recycling rate on a sound statistical basis, as well as quality control of recycling streams. Moreover the collection of industrial data on recycling based on best available technology is essential to predict and calculate the recyclability of passenger vehicles, using the developed models. This chapter will discuss how the developed theory can be used, and models can be calibrated so that these could provide a framework to link recycling to the CAD design software of the design engineer. Some results of the test will be provided to show how this theory can be applied to calculate a statistical recycling rate. Experimental and industrial data on the composition of the car, the separation efficiency of the various processes in the recycling flow sheet, liberation and particle size reduction in the shredder, the quality (or grade) of the recycling (intermediate) material streams is typical information that becomes available through a good understanding of the theory of recycling. This chapter will focus in particular on the data collection and auditing of a physical separation plant within the recycling system, however, keeping metallurgy in mind, which finally has to close the resource cycle of products. It is also discussed how the results of such an experiment could be applied to further simulate (future) recycling scenarios and link physical separation

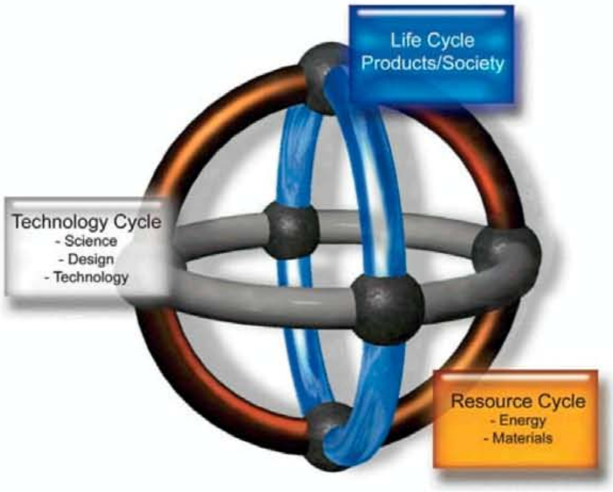


Figure 10.1: Recycling experiments - from theory to practice - combining the Resource cycle and Technology cycle with the Life cycle of the car

plants such as described in this chapter with e.g. thermal treatment of shredder residue. This chapter links the Resource cycle of the material flows throughout the plant (see Figure 10.1) with the Technology cycle of recycling systems (see Figure 10.1). The calculation of the recycling rate in view of EU legislation, which is based on the data that has been collected using the developed models as a technological framework links the Technology and Resource cycle with the Life cycle (see Figure 10.1).

10.2 An industrial recycling experiments

A large scale industrial recycling test has been carried out in which 1153 end-of-life vehicles have been shredded and processed using Post Shredding Technology (PST) processes. The shredding and PST trial was initiated by Auto Recycling Nederland BV, whereas the test was carried out at Comet Sambre, a shredder and PST plant in Châtelet, Belgium [6]. Delft University of Technology [356, 357] was responsible for calculating the batch size, sampling and analysing all the output fractions and setting up the mass balance in order to evaluate Comet Sambre's recycling performance based on the theory as laid down in the previous chapters [356, 6]. One of the objectives of this shredding and PST trial was to determine the recycling rate of cars, which can be achieved using state-of-the-art recycling technology as available at the Comet Sambre shredding and PST plant. The simplified flow sheet of Comet Sambre is given in Figure 10.2 and forms the basis for calculating the recycling rate.

In Chapter 7 (Eq. 7.10) it is stated that the recycling rate of the car is determined by the recovery of each of the materials present in the car. Therefore during a recycling experiment the mass flows within the plant and their composition must be measured and the associated statistics/distribution of the data to be able to properly estimate a statistically accurate recovery of each of the materials composing the car and hence the recycling rate. This section will discuss the procedure by referring to sample size, sample weighing and the

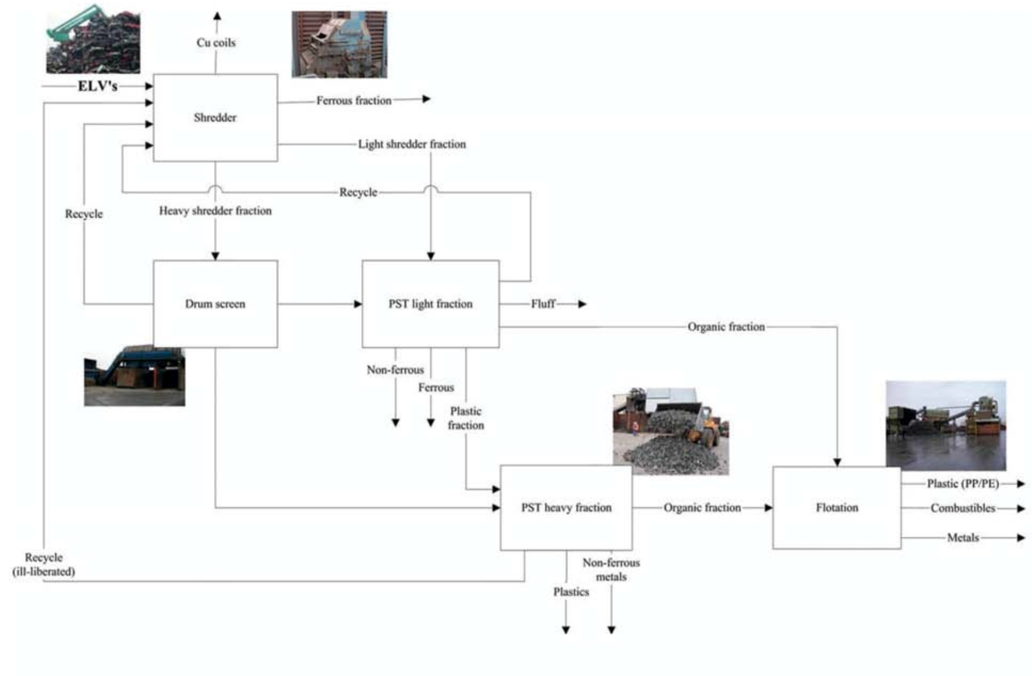


Figure 10.2: Simplified flow sheet of the shredding and PST plant (BAT Best available technology)

sampling procedure, based on the theory as described in Chapters 7 to 9.

10.2.1 Calculation of required batch size of ELV's and sampling for analyses

It can easily be understood that the weight and composition of the ELV's being the input of the shredding and PST trial are all different and therefore the population of ELV's selected determine the statistics guiding the shredding and PST trial and its achieved mass balance and recycling rate. The sampling statistics are defined by Gy's formula [358] relating the sample size of a stream to the accuracy (or standard deviation) of the data to be measured. The input batch size of ELV's to the shredding and PST trial is of crucial importance in the accuracy and therefore statistics of the mass balance, material analyses and the calculation of the recycling rate. Based on Gy's formula (see Eq. 10.2) the required sampling size for the input and all output fractions can be calculated. The calculation of the sampling size is based on the smallest compound to be measured within the output streams (e.g. 0.25% Cu in the steel stream). Moreover also the particle size (see Eq. 10.2) was used as a critical parameter for the calculation of the required batch and sample size, however the critical component for analyses turned out to be the most critical parameter dictating the batch and sample size. This approach is required due to the diverse properties of typical recycling materials as can be seen from Figure 10.3. The calculations were done applying in all cases a standard deviation of 5%. Due to confidentiality the calculations are not presented here, however these are given in the report of the tests by Van Schaik et al. [356]. The influence of dismantling spare parts could be determined accurately based on the data collected from the shredding of the total car as well as following ARN dismantling procedures. From this it is for example possible to prove whether dismantling has a positive effect on the shredding and subsequent operations in view of EU recycling targets.

$$s^2 = \left(\frac{1}{M_{Sample}} - \frac{1}{M_{Total\ sample}}\right) \cdot f \cdot \rho \left(\frac{1}{a_c} - 2\right) \cdot d_c^3 + 0.25 \cdot d_{-95\%}^3 \tag{10.1}$$

where

s	maximum tolerated error of standard deviation (-)
f	shape factor (-)
ρ	density (g/cm^3)
a_c	critical constant to be determined (0-1)
d_c	particle size at a_c (cm)
$d_{-95\%}$	particle size at which 95% lie below (cm)
M_{Sample}	mass of sample to be taken from total (g)
$M_{Total\ sample}$	mass total of sample (g)

Simplifies to the equation below under the conditions of the experiment

$$s^2 = \left(\frac{1}{M_{Sample}}\right) \cdot f \cdot \rho \cdot \left(\frac{1}{a_c} - 2\right) \cdot d_c^3 \tag{10.2}$$

10.2.2 Mass balancing

Mass balances of plants based on measured data mostly do not close due to inevitable weighing and sampling errors, as is also the case for the shredding and PST trial as discussed here.

Figure 10.3: Diverse properties of recycling materials (in which clockwise: steel ca. 650 t. from 1153 ELV's; Cu fraction; Al/Mg/Cu/Zn fraction; plastic fraction; Al/Mg/Cu/Zn fraction; steel fraction)

Data reconciliation is a technique by which the mass balance can be closed by adjusting the process data such as mass flows and analyses within their sampling accuracy. By making use of data reconciliation, the error in the mass balance is assigned to the various measurements and the adjusted data should give a more consistent representation of the actual process. Therefore, data reconciliation can also be used to verify the quality of the measured data, to calculate poor data, as well as to estimate unknown data. There are several methods for data reconciliation described in literature [149]. All methods are based on the principle of minimisation of the adjustments to the experimental data while simultaneously closing the mass balance as defined by Eq. 10.3 and 10.4 and Table 10.1.

$$J(Y) = \sum_i J_i(Y) \tag{10.3}$$

$$J_i(Y) = \left(\frac{M_i - \overline{M_i}}{\sigma_i \cdot M_i}\right)^2 + \sum_k \left(\frac{f_{ik} - \overline{f_{ik}}}{\sigma_{ik} \cdot f_{ik}}\right)^2 \tag{10.4}$$

Table 10.1: Symbols in the objective function of the data reconciliation model

Measured magnitudes	Errors	Adjusted magnitudes
M_i, f_{ik}	σ_i, σ_{ik}	$\overline{M}_i$, $\overline{f}_{ik}$

where

M_i, $\overline{M}_i$	mass of stream i
f_{ik}, $\overline{f}_{ik}$	fraction of component k (steel, aluminium, plastic, rubber, etc.) in stream i
σ_i	estimated measurement error in M_i ('variance')
σ_{ik}	estimated measurement error in f_{ik} ('variance')

Adjustments made to the experimental data do not have total freedom within the range in which variation is possible. Certain restrictions apply to the freedom of the adjustments:

- Material conservation constraints for which the delta is zero applied to all elements, compounds and total mass (Symbols in the objective function of the data reconciliation model)
  - $\sum_i \overline{M}_i = 0$ and $\sum_i \overline{M}_i \cdot \overline{f}_{ik} = 0$
- Data integrity constraints (e.g. the sum of component fractions in a stream should always be 1)
  - $\sum_k f_{ik} = 1$
- User defined constraints such as physics, thermodynamics, grade, recovery, etc.

Mass balances were set up over the in- and output of the 5 different process steps within the shredding and PST trial (see Figure 10.2), as well as over the total flow sheet. Data reconciliation was at first carried out over each of the five process steps in order to derive a closed mass balance on total mass flow as well as for the various components present in the car over each process step based on the measured data. The standard deviation used for the data reconciliation is determined for each stream and analysis individually based on the accuracy of the weighing, sampling and analyses. By comparing the original and adjusted data, the measured data (weights and composition of flows) can be verified. The standard deviation around each dataset together with the standard deviation of the input determines the statistics of the experiment. From the reconciled data of the closed mass balances split factors or recovery values R_{jk} for the various materials k can be calculated for each output stream j over the process steps. A closed mass balance, in which all streams and their composition are given, together with the corresponding standard deviation, is the only reliable basis on which a recycling system can be evaluated, split factors (process efficiency) can be derived, the grade of recycling (intermediate) products can be determined, and the recycling rate can be calculated. Therefore, the reconciled data, resulting in a closed mass balance on both total mass flow and component level forms the basis for any further calculation resulting from the test.

10.3 Weighing, sampling and analyses of material flows

10.3.1 Characterisation of input (1153 ELV's)

The recycling rate of passenger vehicles is determined by various statistically distributed parameters, such as the design of the car [356]. Therefore the calculation of the recycling rate based on this large scale industrial trial should take cognisance of the statistical nature of the recycling rate. The statistics of the recycling rate are determined by the standard deviation of the measured data (weight and composition of material flows), as well as by the statistics of the input of the test. Each of the 1153 end-of-life vehicles was weighted before the trial revealing the weight distribution. Moreover the vehicles were visually inspected before the trial to make an inventory of missing parts. The composition of the cars (as well as of the missing parts) is known from ARN databases. The input of the test is therefore very well defined, which is crucial to derive an accurate mass balance, with its corresponding statistics. Figure 10.4 shows the weight distribution of the 1153 cars being the input of the test.

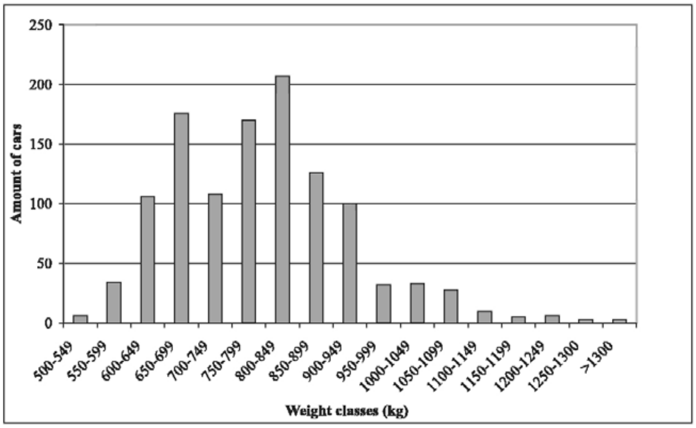


Figure 10.4: Weight distribution of the 1153 ELV's

10.3.2 Weighing of the material streams

Data collection on all material flows makes it possible not only to set up a mass balance over the total flow sheet, but also over the 5 different process steps as can be seen from Figure 10.2 (shredding, drum screen, Light Fraction treatment, Heavy Fraction treatment and Flotation). If a proper and statistically sound mass balance is to be set up that also provides information on the intermediate streams, data cannot be simply collected on the output of the total flow sheet as has been the case in practice up till now for similar (although smaller) tests. It must be measured over all steps i.e. on the input, intermediate and output streams, in order to increase the amount of data available for data reconciliation, which increases the accuracy of the mass balance and its statistics. Furthermore, if efficiencies (recovery factors) of the various process steps have to be determined to use in the calculation including the recycling streams within the plant, no other way for data collection (weighing and analysis) than proposed here is possible. All weighing was done by a front-end-loader equipped with a load cell on the shovel (Figure 10.5) or by truck on the weighing bridge.

10.3.3 Sampling

Gy's formula is used to calculate the required sample size for each individual material flow in order to carry out reliable analyses, based on particle size, critical component to be analyzed, shape factor of the particles etc. as defined by Eq. 10.2. This equation dictates the weight of each sample. The sampling was taken in-line by front-end-loader to the magnitude as calculated by Gy's formula as shown in Figure 10.6.

10.3.4 Procedures on the plant during sampling

The procedures on the plant involved a strict set of rules dictated by a protocol set up for the tests. All samples were collected in cleaned areas Figure 10.7(a), containers etc. and marked given individual numbers and labels Figure 10.7(b).

Figure 10.5: Weighing the ferrous sample by Volvo front-end-loader

Figure 10.6: Creating a composite sample from in-line sampling with the front-end-loader


(a) (b)

Figure 10.7: (a) Cleaned areas before each trail in this case for the drum screen and (b) labeling of all samples and streams with a consistent code (white sign post at back)

Figure 10.8: Analyses of the material flows by hand sorting in the authors' laboratory

10.3.5 Analyses of material flows

The calculation of the mass balance by data reconciliation (Eqs. 10.3 and 10.4) and recycling rate not only requires data on the total weight of the material flows within the plant, but also the composition of each stream. A large body of data renders the mass balance more accurate and makes it possible to calculate the recovery for each of the different materials over the various process steps. Eq. 7.10 (Chapter 7) indicates that the recycling rate of the car is determined by the recovery of each of the materials and the statistics are affected by the standard deviation on the composition of the various material flows.

Hand sorting

The samples of all the material flows were analyzed to determine their material composition by the use of hand sorting into fractions of the numerous materials composing the car. The composition is consistently measured over all streams, so that a mass balance can be set up for all (main) materials composing the car. This was performed by up to ten employees/students of the department at a time as can be seen from Figure 10.8.

(a) (b)

Figure 10.9: (a) The X-ray Fluorescence equipment used to analyse all the fine samples, (b) The XRT equipment used to analyse the samples for accuracy and un-liberated material

Sink/float tests

Since hand sorting is not selective enough for some materials, additional separation is performed on the relevant streams. Density separation (heavy medium sink-float) using a Sodium Polytungstate solution has been carried on aluminium/magnesium mixtures produced by hand sorting, since it is very difficult to make a visual distinction between these two metals. The density separation is also applied to analyze the organic fractions in combination with hand sorting.

XRF-analysis

The material flows with a very small particle size distribution (between 0-4 mm) have been analyzed using XRF-analysis (X-ray Fluorescence, Figure 10.9).

Steel converter

40 tons of the ferrous fraction were analyzed by an industrial steel converter at a Belgium steel plant. The ferrous fraction was mixed with liquid steel units (including pig iron) of known composition. Based on the composition of the liquid steel of known composition and added alloying elements the composition of the ferrous scrap is back-calculated from the analyses of the final smelting results. This analysis was conducted in duplicate.

Quality control by means of other equipment

The quality of hand sorting was also controlled by making Dual X-ray transmission scans of the hand sorted materials (Figure 10.9)b. XRT images were made from both the sampled stream from the plant as well as the numerous material fractions after hand sorting in order to control the material content of the sorted fractions, whereas the XRT scans of the unsorted sample gives an indication of the composition of the stream before analyses.

Figure 10.10, Figure 10.11 and Figure 10.12 show the normal pictures and XRT images of three different fractions viz. plastic fraction (Figure 10.10), Al/Mg fraction (Figure 10.11) and an un-liberated fraction (Figure 10.12) all three after hand sorting. The XRT image of the plastic fraction (Figure 10.10(b)) shows that the plastic fraction is free of other materials, but

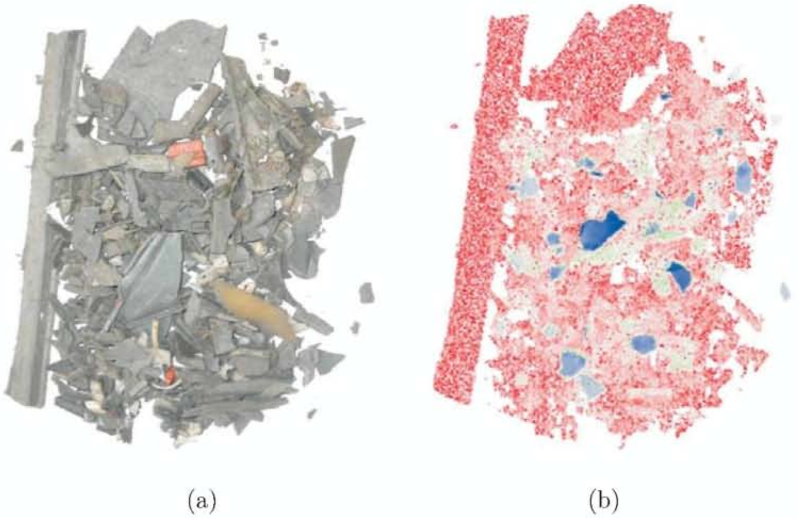

(a) (b)

Figure 10.10: Plastic fraction after hand sorting; (a) normal picture; (b) XRT image

contains flame-retardant plastics (dark blue) as well as PVC (pink). Figure 0.12 (a) shows a picture of an Al/Mg fraction after hand sorting. The XRT scan of Figure 10.11 (b) makes clear that the Al/Mg fraction still contains some other (heavy) metals (dark blue particles). Based on the knowledge that the ferrous components have been removed by a magnet during hand sorting; the dark blue colour in the XRT scan (see Figure 10.11 (a)) suggests that the Al/Mg fraction is contaminated with stainless steel (stainless steel can have a similar appearance as wrought aluminium). This is once again evidence of poor design since not all materials were liberated during shredding. Figure 10.12 (a) shows a picture of un-liberated particles. The XRT scan of this material (Figure 10.12 b)) shows that the particles contain more than one material, e.g. the rubbers contain a core of steel, whereas some of the plastics contain steel bolts. It becomes clear from Figure 10.12 (a) and (b) that this can never be separated by (hand) sorting. However during hand sorting estimation is made of the composition of the un-liberated particles in combination with the XRT images of the material.

10.4 Calculation of mass balance on such an experiment

The calculation of the recycling rate was carried out in various steps. Each of the different steps required are discussed below in separate sections. Due to confidentiality only selected data of the experiment is provided for illustration of the methodology. The data is presented in the report of the tests [356].

10.4.1 Data reconciliation

Mass balances were set up over the in- and output of the 5 different process steps within the shredding and PST trial (see Figure 10.2), as well as over the total flow sheet. Data reconciliation was at first carried out over each of the five 'black boxes' in order to derive a

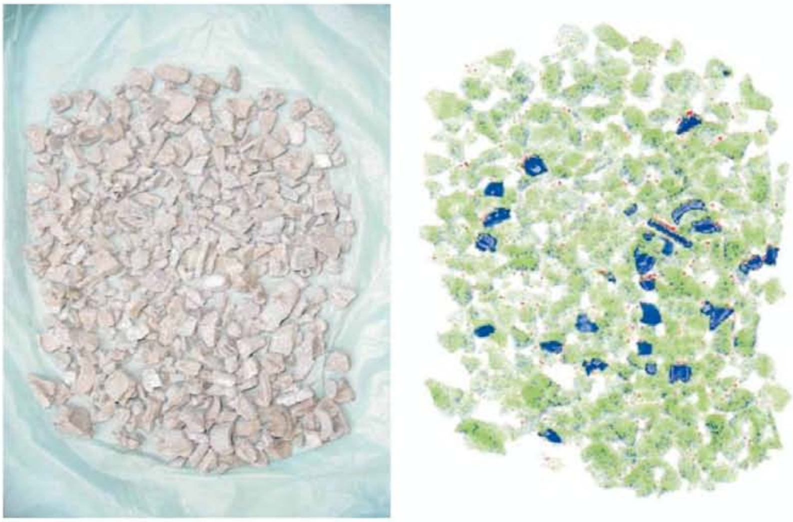


Figure 10.11: Al/Mg fraction after hand sorting; (a) normal picture; (b) XRT image

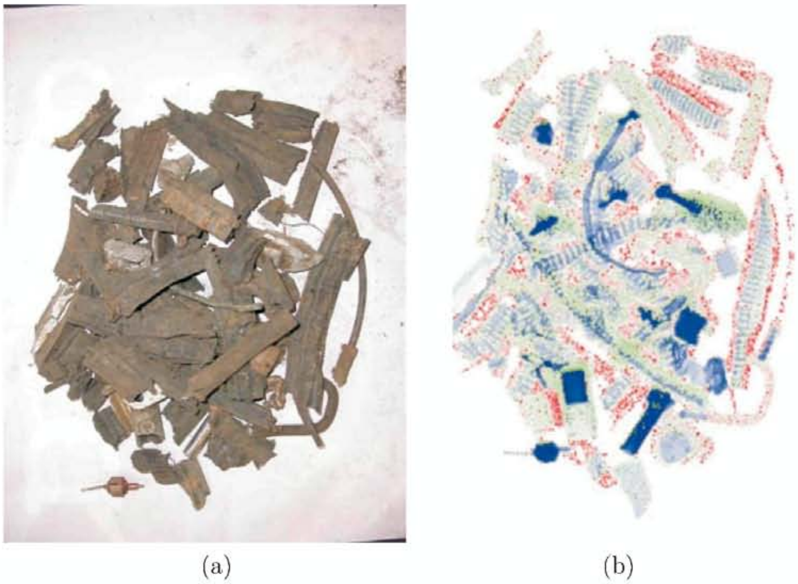


Figure 10.12: Un-liberated fraction after hand sorting; (a) normal picture; (b) XRT image

closed mass balance on total mass flow as well as for the various components present in the car over each process step (which is regarded as a black box due to confidentiality) based on the measured data. The standard deviation used for the data reconciliation is determined for each stream and analysis individually based on the accuracy of the weighing; sampling and analyses (see Table 10.2 for the Heavy fraction treatment). Moreover the original and adjusted weights and composition of the various flows throughout the plant as a result of data reconciliation is given in Table 10.2 for the Heavy fraction treatment (obviously similar Tables have been derived for the other process steps). By comparing the original and adjusted data, the measured data (weights and composition of flows) can be verified. The standard deviation around each dataset together with the standard deviation of the input determines the statistics of the experiment.

10.4.2 Recovery (split) factors

From the reconciled data of the closed mass balances split or recovery factors R_{jk} for the various materials k can be calculated for each output stream j over the different process steps as illustrated in Table 10.3 for the Light fraction treatment. The split or recovery factors for both the total mass flows as well as for the mass flow for each component are subject to the standard deviation of the weighing, sampling and analyses and are therefore of a statistically distributed nature. The recovery or split factors express the process performance. Moreover, by calculating the recovery or split factors the material flows throughout the plant can be traced. Once again due to confidentiality only a small selection of results is presented, however, note the components analysed for. These components were consistently analysed for, for each of the material flows in the plant. All mass flows and analyses around each of the process steps are given in Van Schaik et al. (2004)[356].

Simulation of recycling scenarios

The recovery or split factors can be used to predict recycling scenarios e.g. for a changing input. The calculated recovery (split) factors can be applied to further develop the modelling and simulation of recycling scenarios in order to e.g. simulate the distributed and time-varying composition of the automotive shredder residue, which can become input of thermal processing in future. A model based approach as discussed in the previous chapters, calibrated by proper industrial data is indispensable in order to assess the feasible of further (thermal) treatment of shredder residue. These predictions must be considered with care, since the performance of unit operations is dependent on the size distribution and composition of the input. Therefore solid knowledge on the behaviour of the different processed as a function of the composition and size distribution of the feed is essential.

Calibration of models

The recovery or split factors as derived from the experiment are directly linked to the models as discussed in Chapter 8 (see Eq. 8.11 and 8.12). Moreover this data can be applied for calibration of the models.

10.4.3 Grade of recycling (intermediate) products

The grade or quality of the recycling (intermediate) products determines the possibility of the material to be absorbed by the market or industrial recycling or plastic recovery processes. Moreover the grade of the material flows gives an indication of the process and plant

Table 10.2: Original data, standard deviation and adjusted data on mass flows and composition on the Heavy fraction treatment (based on the mass balance per process step)

Heavy fraction treatment		M_i (kg)	$\overline{M}_i$ (kg)	σ_i (%)	$f_{i,steel}$ ( )	$\overline{f}_{i,steel}$ ( )	$f_{i,Al}$ ( )	$\overline{f}_{i,Al}$ ( )	$f_{i,plastics}$ ( )	$\overline{f}_{i,plastics}$ ( )	$f_{i,...}$ ( )	$\overline{f}_{i,...}$ ( )	σ_{ik} (%)
Input	22	30340.0	30119.5	0.5	0.0588	0.0619	0.5100	0.4588	0.1677	0.1802	...	...	5
Output	25	2054.0	2049.0	0.5	0.7717	0.7715	0.0742	0.0744	0.0165	0.0165	...	...	5
	...	...	...	...	...	...	...	...	...	...	...	...	...
	...	...	...	...	...	...	...	...	...	...	...	...	...
	...	...	...	...	...	...	...	...	...	...	...	...	...
	...	...	...	...	...	...	...	...	...	...	...	...	...
	28	15080.0	15347.0	0.5	0.0051	0.0051	0.8671	0.8699	0.0138	0.0138	...	...	5

Table 10.3: Recovery or split factors R_{jk} for the Light fraction treatment given for some components are calculated from the reconciled mass balance for the Light fraction treatment (based on the mass balance per process step)

Light fraction treatment													
					Light fraction treatment								
j	Total mass	Steel	Al	Plastics	Zinc	Brass	SS	Cu	Rubber	Foam	Textiles	Wood	Glass
5	0.45	0.03	0.00	0.18	...	...	...	...	...	...	...	...	...
6	0.01	0.00	0.00	0.02	...	...	...	...	...	...	...	...	...
...	...	...	...	...	...	...	...	...	...	...	...	...	...
...	...	...	...	...	...	...	...	...	...	...	...	...	...
...	...	...	...	...	...	...	...	...	...	...	...	...	...
20	0.03	0.15	0.29	0.01	...	...	...	...	...	...	...	...	...

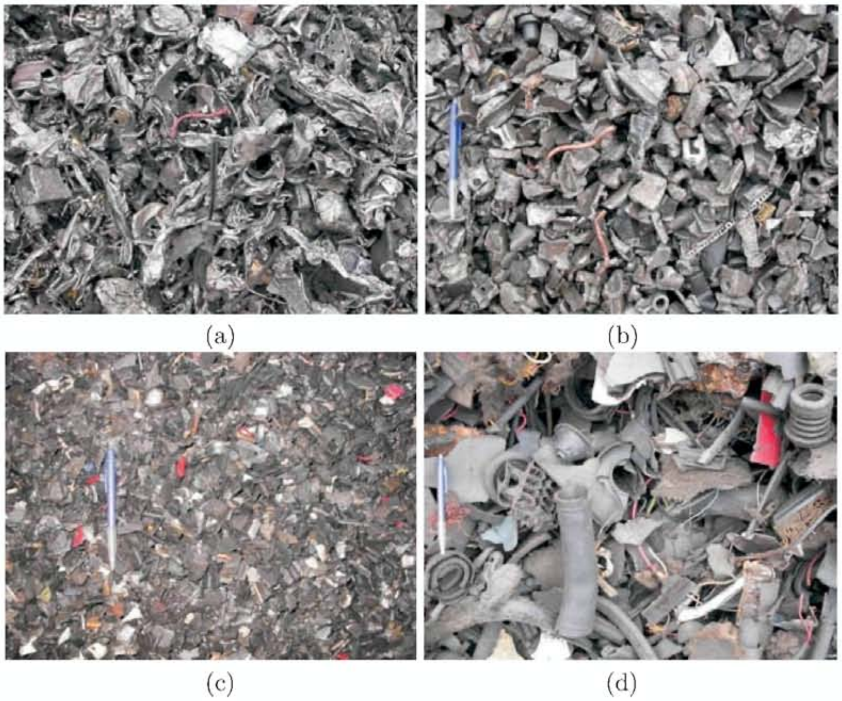
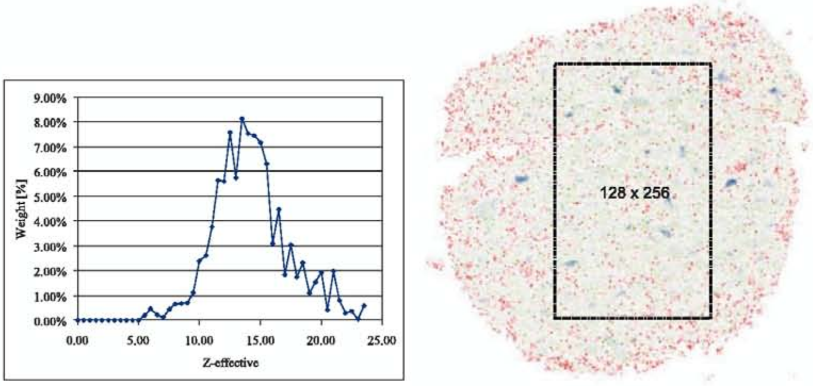


Figure 10.13: Grade of different recycling (intermediate) products; (a) steel fraction; (b) non-ferrous metals fraction (mainly aluminium); (c) plastic fraction; (d) rubber fraction

performance. The grade of the various material flows within the Comet Sambre plant was determined for each of the streams by analyses as discussed above (hand sorting/sink float separation/XRF and XRT analysis). The analyses were carried out to be able to set up a closing mass balance on component level over all process steps within the Comet Sambre plant, however it reveals also the distribution of the grade/quality of the different streams as a consequence of imperfect separation. As can be seen from Figure 10.13 a process is never perfectly selective and will never produce a stream with 100% grade within one step, due to the inseparable relationship between grade and recovery as discussed in Chapter 8 (see Eq. 8.9 to Eq. 8.11).

As discussed above all streams and hand sorted fractions were analysed using the XRT scan. The z-effective (effective atomic number) as derived from the XRT scans of the various material streams can be presented as shown in Figure 10.14 for the aluminium/magnesium fraction of the PST heavy fraction. Figure 10.14 (a) shows the distributed nature of the z-effective measured for each of the material flows, whereas Figure 10.14 (b) gives the XRT image of the material. The distribution in the z-effective values measured for the material streams, gives an indication of the different materials present in the stream (each with their specific z-value) Therefore the standard deviation of the z-effective distribution can give an indication of the grade/quality of a stream (but also of the analyses) depending on the material type (Figure 10.10 (b) shows that a pure plastic fraction can have a large standard deviation in the z-effective due to the presence of e.g. flame retardants or PVC). Figure 10.15 (a)



(a) (b)

Figure 10.14: (a) Distribution of z-effective for the aluminium/magnesium fraction from stream 28; (b) XRT image of the aluminium/magnesium fraction from stream

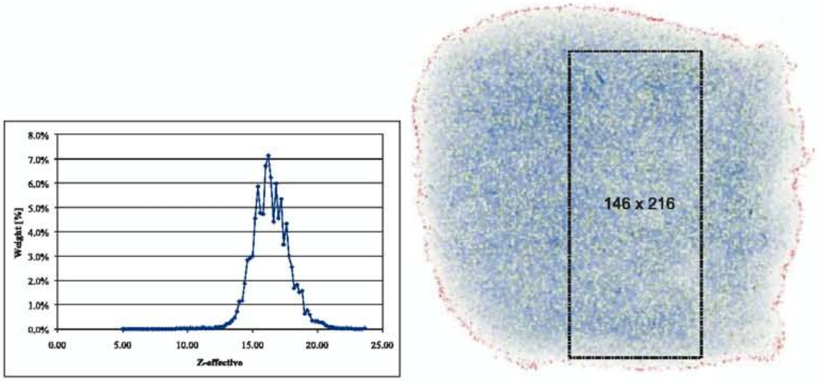
shows the determined z-effective for one of the fine material streams (mineral fraction) and the corresponding XRT image Figure 10.15(b)).

10.4.4 Samples on material flows

During the test, samples were taken from each of the streams (intermediate and output) in the plant. The substantial sample sizes led to mass differences between the output of the one process step and the input of the same stream to another process step (e.g. the heavy shredder fraction coming from the shredder, which is the input of the drum screen, see Figure 10.2). Therefore, the mass balance could at first only be set up over the 5 process steps individually and not over the total flow sheet. The weight of the samples and their corresponding composition have to be added to the total (reconciled) mass flows in order to achieve a correct mass balance, which is related to the input weight of the 1153 end-of-life vehicles, permitting a correct calculation of the recycling rate. The split factors of Table 10.3 have been applied to recalculate the mass flows within the plant including the mass and corresponding composition of the samples. Since the mass balances could not be set up initially over the total flow sheet due to the batch nature of the plant and the sample weights removed from the various streams between the different process steps, data reconciliation has to be performed to progress from the mass balance over the different process steps (Table 10.2 and Table 10.3), to the closing mass balance over the total flow sheet. The data reconciliation adjusts the masses and compositions over the total flow sheet according to their accuracy in order to close the mass balance over the total flow sheet, while simultaneously the mass balances over the different process steps remain closed. The adjusted mass and material flows (composition) as a result of the data reconciliation are given in Table 10.4. The adjustment of the mass and material flows in order to close all mass balances will obviously lead to a slight redefinition of the split factors.

Table 10.4: Original data, standard deviation and adjusted data on mass flows and composition on the total flow sheet (including sample weights) for the Light fraction treatment

Light fraction treatment		M_i (kg)	$\overline{M}_i$ (kg)	σ_i (%)	$f_{i\,steel}$ (-)	$\overline{f}_{i\,steel}$ (-)	$f_{i\,Al}$ (-)	$\overline{f}_{i\,Al}$ (-)	$f_{i\,plastics}$ (-)	$\overline{f}_{i\,plastics}$ (-)	f_i (-)	$\overline{f}_{i\,...}$ (-)	σ_{ik} (%)
Input	1	149927.5	151755.3	0.5	0.0251	0.0228	0.0046	0.0045	0.2026	0.2176	...	...	5
	21	40277.3	40244.7	0.5	0.0228	0.0279	0.3342	0.2677	0.2538	0.2465	...	...	5
Output	5	86080.0	86135.6	0.5	0.0020	0.0019	0.0000	0.0000	0.0868	0.0895	...	...	5
	...	...	...	...	...	...	...	...	...	...	...	...	...
	20	6671.1	6671.4	0.5	0.1135	0.0968	0.4973	0.5011	0.0480	0.0480	...	...	5



(a) (b)

Figure 10.15: (a) Distribution of z-effective for the mineral fraction; (b) XRT image of the mineral fraction

10.4.5 Standard deviation

The measured standard deviation around each data point (mass and element flows) are used in the least-square fit to reconcile the mass balance around each individual unit operation in the plant as well as over the total flow sheet, within the statistics of the collected data. This is the opposite of what is done in Chapter 7, where identical normal distributions and corresponding standard deviations are assumed for each data point, whereas the standard deviation is known from the data collection. The recovery or split factors as derived from the closed mass balance have a standard deviation, which is a subject to the standard deviation of the mass and element flows on the plant. Therefore, the standard deviation of the recycling rate calculated from the reconciled mass balance is a complex function of the statistics around the mass and element flow as well as the grade and recovery.

Input (missing parts)

Although very limited, inevitably some parts of the cars were missing like e.g. mirrors. An inspection was carried out on each of the 1153 cars wrecks, input of the test [356]. The cars were weighted and inspected on composition; the missing parts of each car wreck (e.g. mirrors, doors, etc.) were registered. The actual recycling rate of end-of-life vehicles based on this shredding and PST trial should be calculated on the weight of complete end-of-life vehicles (weight and corresponding composition). In order to calculate the recycling rate based on complete ELV's, the actual input weight and composition of the tests have to be recalculated to a complete ELV's including the missing parts, from which the weight and composition is known from the ARN database. Using the split factors calculated from the data reconciliation over the total flow sheet, the mass balance (for total mass flows as well as for the components) was calculated for complete ELV's to serve as the basis for the determination of the recycling rate.

10.4.6 Recycle streams

In the normal operation of the shredding and PST plant streams are being recycled to the shredder in order to reduce the particle size or re-shred the un-liberated materials. As within the shredding and PST trial this was not possible from a practical point of view, some streams are present in the mass balance as output streams, which would normally find their way back to the shredder and PST plant. To be able to calculate the recycling rate properly, these recycle streams have to be included in the calculations of the mass flows. Since no data could be measured on the behaviour of these material flows and their corresponding composition in the shredder and the PST plant, the redistribution of these streams and their composition had to be estimated using the measured data from the reconciled mass balance, i.e. the recovery or split factors are used to recalculate the mass balance over the shredder and PST plant. The recalculation of the final mass balance can also be carried out based on data reconciliation over the total flow sheet of the trial (see Figure 10.2) including the recycle streams. It must however be noted that due to the lack of measured data on the recycle streams, this can never be simulated 100% accurately, but is the only possible approach to be able to include the recycle streams in the mass balance. The mass balance over the total flow sheet, including sample weights and recycle streams based on the input of complete ELV's forms the basis for the calculation of the recycling rate and the determination of its statistics.

10.5 Practical calculation of the recycling rate from the recycling experiment

The mass balance derived from the data of the shredding and PST trial for complete ELV's over the total flow sheet, including the sample weights and taking cognisance of the recycle streams within the flow sheet forms the basis for the calculations of the recycling rate. Moreover the composition of the various (output) flows defines the quality of the output streams, which determines the possibility of the application of the produced output streams.

10.5.1 De-pollution

The weight and composition of the 1153 ELV's, being the input of the test, have been determined based on the weighing of the car wrecks and the ARN database. The car wrecks being the input of the test have been de-polluted before shredding according to legislation (Decree of 24 May 2002). The materials for de-pollution (battery, oil, cooling liquid, brake fluid, tires, inner tubes, windscreen washer fluid, LPG-Tanks, fuels, oil filter) were not part of the input of the test and are therefore not included in the mass balance as described above. In order to calculate the recycling rate of the complete vehicle, the recovery of the materials for de-pollution has to be included in the calculations.

10.5.2 System boundaries

The definition of the system boundaries is important for the calculation of recyclability and recoverability rates. System boundaries I and II can be defined for the determination of the recycling and recovery rate, see Figure 10.16.

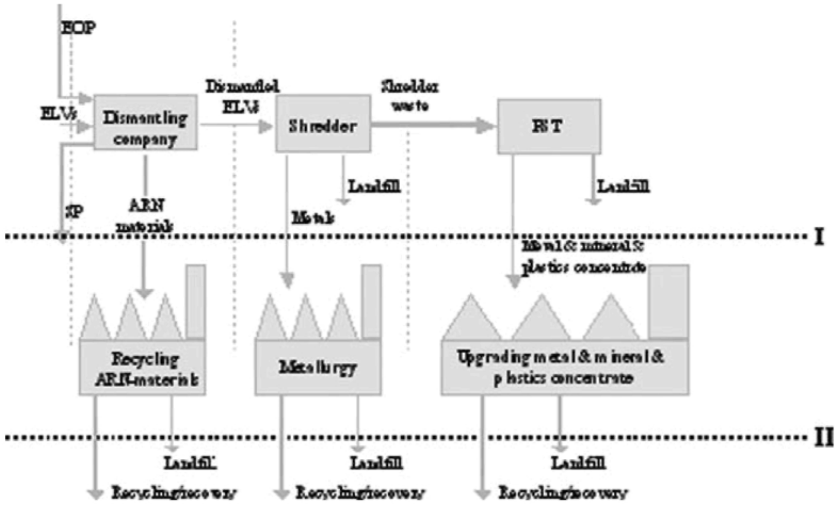


Figure 10.16: ELV recycling chain with system boundaries

System boundary I

In the calculation of recyclability and recoverability a 100% yield is assumed for the materials entering the recycling or recovery process.

System boundary II

Of critical importance to reach recycling targets set by legislation is the quality control of recycling intermediate products created during shredding and physical separation, which ensures that the feed to metal producing processes permits the economic production of quality metal products. Therefore for each of the recycling and recovery processes the recovery per material should included in the recycling rate in order to include the losses in the process for:

- The recoveries for the recycling of C1 materials and tyres based on data of the ARN recycling companies;
- The metal recovery within metallurgical operations (e.g. aluminium melting operations, EAF, etc.) for the processing of recycling intermediate streams coming from the shredder and PST processes (see Eq. 8.13, Chapter 8);
- The recovery/efficiency of further processing of the mineral/plastic concentrates after the PST processes.

The calculation of the recycling/recovery rate achieved for the shredding and PST trial can hence be defined based on System boundaries I and II.

10.5.3 Procedure for the calculation of recycling/recovery rate and corresponding statistics

Based on the mass balance as presented and discussed above, the recycling rate of end-of-life vehicles based on the test can be calculated. Ultimately the recycling rate is determined by the possibility of the market to absorb the produced output streams (either for direct application or in metallurgical or thermal processes) and is therefore partially determined by the geographic location of the plant. The recycling rate can therefore be calculated based on the mass balance and valuable produced output streams of the plant under consideration. The recycling rate derived from this experiment would be based on the Belgium situation and market conditions.

10.5.4 Recycling and recovery rate

The recycling rate achieved as calculated from this experiment is above 85%, consisting of material recycling and energy recovery. The accuracy of recycling and recovery rate achieved is a function of the accuracy of the total experimentally determined mass balance, which is 0.3%. The quality of the output streams, which determine the possibility for selling these streams, is subject to the accuracy of the analyses of the composition of the material flows, which is 5%, as also used in Gy's formula. Once again, due to confidentiality the full calculations giving the recycling rate could not be presented here, but are however presented in the confidential report on the tests [356].

10.5.5 Data for model calibration

The recovery or split factors, as well as data on the grade or quality of the (intermediate) material flows as collected from the experiment are directly linked to the models as discussed in Chapters 8 and 9. Furthermore, the data on particle size distribution and liberation (as discussed in Chapter 9) can be used in the models of Chapter 8 and 9. This type of data collected from industrial practice on the basis of best available technology can be applied for calibration of the models and is crucial to calculate and predict the recycling rate, also in view of the type-approval of passenger vehicles.

10.6 Discussion

It was discussed in the previous chapters that the definition of the recycling rate and the understanding of its leading parameters can only be fully captured on the basis of various models, describing different levels of the resource cycle and recycling system, thus providing information on the dynamic and distributed nature of the resource cycle as well as on the detailed modelling of the recycling system and the role of this in realizing high recycling rates. The recycling rate is determined by the recovery rate for each of the individual components/materials present in the car. The efficiency (recovery factors) of the various unit operations within in the recycling system, together with the properties of the materials to be processed determine the recovery for each of the individual materials and therefore the maximum achievable recycling rate.

- It is of crucial importance for the application and reliability that useful data is available for the calibration of the models developed in this Part, all within the statistical limits of sampling and mass balancing. Up to now, due to poor theoretical understanding of recycling systems, these data have not been available and have not been collected in a proper manner. Therefore experiments have to be performed on a plant to gather data for calibration.

- The developed theory provides a fundamental basis for the assessment of recycling systems, data collection on recycling systems as well as to calculate the recycling rate of products, in this case the car.
- Based on the theory developed, this chapter discusses the methodology how recycling systems should be assessed in practice illustrated on the basis of a large scale recycling experiment, in which 1153 ELV's were recycled. It is discussed how data should be measured and how mass balances should be reconciled within the framework of statistics in order to calculate the recycling rate of end-of-life vehicles with a standard deviation and to calibrate the developed models.
- It is illustrated that the application of classical theory of sampling and data reconciliation is required to set up closing mass balances over the plant and its unit operations as well as to calculate statistically correct sample sizes for analyses of the various material flows throughout the plant.
- From the reconciled and therefore closed mass balances for both mass and element flow, the recovery (or split) factors for each element over the various process steps throughout the plant as well as the quality of all (intermediate) material flows could be determined, subject to the statistics of the mass and element flows within the plant. The recovery factors as well as the measured grade of (intermediate) recycling products as derived from the data on the plant data can be used for calibration of the recycling optimization models.
- The recovery (split) factors as derived from the experiment can be used to simulate possible recycling scenarios, calculate the recycling of (future) cars and inherently calculate the composition of various (intermediate) recycling products, which determines the possibility to bring the recycling products into the market. These models could be applied to e.g. determine the distributed and time-varying composition of the automotive shredder residue in order to study the possible treatment of this fraction in thermal processing plants as a function of changing design and recycling scenarios.
- This chapter suggests that a proper methodology and standard for the determination of the recycling rate can only be determined if a solid theoretical basis (as discussed in the previous chapters and applied in this large scale recycling test) has been developed and adopted by the industry.
- The tests illustrate that the recycling rate can never be a single value be should always be reported in combination with the error margin. Without the standard deviation or error margin, any calculation of the recycling rate is meaningless. This means that tests performed up till this experiment, are strictly speaking useless.
- The approach used to evaluate the results for the recycling of 1153 cars in Belgium discussed in this chapter is the first time this has been done with such a theoretical rigor in such an experiment.
- The procedure as discussed in this chapter is the only manner in which statistically reliable recycling rates can be calculated. If statistically and legally reliable results are to be achieved in future experiments to determine the recycling rate of cars or any other product under consideration, the methodology as presented here should become the norm! Anything less can be contested in a court of law since there is no fundamental and reliable basis for the calculation of recycling rates as presently defined by

EU legislation. In short therefore, present recycling legislation is flawed as is the ISO norm for calculating recycling rates, since it does not at all take into consideration the statistics of the data, nor does it take the integrity of the data over the whole chain in to consideration, neither does it demand a closed mass balance.

10.7 Examples and case study

10.7.1 Calculate sample size for an ELV steel sample

Calculation of required sample size for the ferrous fraction arising from the shredder.

$$s^2 = \left(\frac{1}{M_{Sample}}\right) \cdot f \cdot \rho \cdot \left(\frac{1}{a_C} - 2\right) \cdot d_c^3$$

Data

s $= 0.05$
f $= 0.5$
ρ $= 7$ g/cm$_3$
a_c $= 0.0025$ (0.25% Cu)
d_c $= 4$ cm

Answer

$$M_{Sample} = \left(\frac{1}{0.05^2}\right) \cdot 0.5 \cdot 7 \cdot \left(\frac{1}{0.0025} - 2\right) \cdot 4^3 = 35.7\,\text{tonne}$$

10.7.2 Definition of the ISO norm and monitoring protocol for the calculation and prediction of the recycling rate of end-of-life vehicles

Background

The European Union directive on the recycling of passenger vehicles (Directive 2000/53/EC, 2000), imposes strict recovery and recycling targets to be achieved in the nearby future. Calculations to predict the recyclability of the car are required for the type-approval of cars (COD 2004/0053, 2004), which have to obey to the targets as laid down in the EU directive on passenger vehicles (Directive 2000/53/EC, 2000). In view of these legislative constraints, it is essential that the recycling rate of the car can be calculated and predicted. The International Organization of Standardization (ISO, 2002) has defined a calculation method for the recyclability/reusability and recoverability/reusability rate of road vehicles to be used as an international standard for assessing the ability of new vehicles to be recovered/recycled. However, the recyclability and recoverability rate are simply defined as the ratio between the sum of the mass of materials reused/recycled/recovered during dismantling, metal separation and non metallic residue treatment and the 'complete vehicle kerb mass' at end-of-life defined in ISO 1176 (ISO, 1990). The calculation method presented by the International Organization of Standardization is a single value, static approach, which is not based on detailed knowledge of end-of-life separation technology and metallurgical

processing as the basis for the defined variables in the recyclability/recoverability rates (e.g. the metal content is considered as being fully recyclable, which is not the case due to prevalent physics, thermodynamics and kinetics).
Therefore it is not valid to use this ISO norm as a basis to assess recycling performance and calculate the recycling rate in practice in view of the EU directive on end-of-life vehicles.

Definition of the ISO norm and monitoring protocol

Define a new 'ISO norm' for:

- the calculation of the recycling rate of (new) multi-material cars;
- the assessment and monitoring of recycling scenarios;

in view of the targets laid down in the ELV directive (Directive 2000/53/EC, 2000).

Make sure that the following issues are addressed:

- The method should be defined based on theoretical knowledge on the complex behaviour of recycling processes, separation efficiency (physics), thermodynamics, etc.
- The effect of choices made by the material scientist must become clear, by addressing the complex interaction between the design of the car, material choices, material connections, joining types etc. and the final material recovery over time.
- Include the role of statistics, distributed properties of the design and use, and statistics of monitoring and measuring on a recycling plant in your protocol.

10.7.3 Design of a monitoring optimization model

In view of the recovery/recycling targets of 85%/80% (2006) and 95%/85% (2015) to be achieved for end-of-life vehicle recycling according to the EU directive (Directive 2000/53/EC), the questions should be asked: "How can the recycling of ELV's be monitored in an objective way, in order to investigate and communicate the feasibility of the EU directive on ELV's and calculate the recycling rate". Moreover, with regard to the type-approval of cars for recycling (COD 2004/0053, 2004), calculations to predict the recyclability of the car are required to prove that a new car design obeys to the targets as laid down in the EU directive on passenger vehicles (Directive 2000/53/EC, 2000).

The International Organization of Standardization (ISO, 2002) has defined a calculation method for the recyclability/reusability and recoverability/reusability rate of road vehicles to be used as an international standard for assessing the ability of new vehicles to be recovered/recycled.

In the case study in Section 10.7.2, you have critically reviewed and redefined this ISO norm, since the calculation method presented by the ISO norm is a single value, static approach, which is not based on detailed knowledge of end-of-life separation technology and metallurgical processing as the basis for the defined variables in the recyclability/recoverability rates (e.g. the metal content is considered as being fully recyclable, which is not the case due to prevalent physics, thermodynamics and kinetics). Therefore the current ISO norm and even the EU directive is not suitable to asses and monitor the recycling performance and calculate the recycling rate in practice in view of the EU directive on end-of-life vehicles. Moreover, these cannot be used to evaluate and compare various recycling scenarios or recycling plants. A proper fundamental modeling basis is required to do this.

A common language for the monitoring and determination of the recycling rate can only be established if these fundamental theoretical models are developed, used and adopted by the industry and EU in order to calculate statistically and fundamentally reliable recycling rates. These fundamental recycling models take into consideration (i) material quality; (ii) separation physics and thermodynamics; (iii) losses and emissions; (iv) plant/flowsheet architecture; (v) distributed and dynamic properties, of present and future car designs. This permits:

- Monitoring of recycling systems in view of EU legislation;
- Calculation of the recycling rate of (new) multi-material cars;
- Assessment of present recycling plants/recycling schemes;
- Evaluation of different recycling routes;
- Evaluation of the feasibility of the recycling targets of the EU;

in view of the targets laid down in the ELV directive.

Recycling system design for monitoring

As a continuation of the ISO norm case study, your task is the following:

- Design a recycling system model for the monitoring of EU recycling legislation. This recycling system optimization model should be able to:
  - Describe mass flows through the system;
  - Calculate the quality of each of the (intermediate) recycling streams;
  - Evaluate the performance of different 'scenarios' as a function of an appropriate objective function and constraints;
  - Establish an optimal architecture for the flow sheet using the processes given as a function of an appropriate objective function and constraints;
  - Calculate the recycling rate per material stream as well as for the total car.
- Recycling system model: In order to design this model you have to address the following topics:

  Set up a flow sheet of the total recycling system, in which you can define different 'scenarios' by varying the structural parameters of your flow sheet. Add the end-processing of plastics to this flow sheet.

  Define mass balance and/or including separation efficiency equations for:

  * The major materials/minerals composing the car (Al, Steel, Cu, Plastics, Foam) and their corresponding elemental composition
  * Particle size classes (0-2 mm, 2-20 mm, 20-50 mm, 50-100 mm, ¿100 mm)
  * Liberation classes of the minerals (define 5 liberation classes)
  * Each of the processes (i) within your flow sheet

Define the following variables/parameters (Please give technological, practical and economical arguments for all the assumptions you made when defining the above):

  - Split- or recovery factors for each of the processes for each separate material and/or element, particle size class and liberation class in your recycling flow sheet in terms of ranges for the optimization model
  - Composition (matrix) of the different liberation classes for the various materials/minerals present in the car
  - Composition of the car
  - Define appropriate constraints for the input quality of your metallurgical processes
  - Assume a particle size and liberation class distribution after shredding as the input for your flowsheet (do not model the shredding step)

Subsequently convert all this into an AMPL model and submit the AMPL model (*.mod) and data file (*.dat) and commands file (*.run) to the NEOS server. (see explanation below)

- Case studies/examples
  - Define two different 'scenarios' from your flow sheet by making certain structural parameters 0 or 1. Evaluate the performance of these two different 'scenarios' based on the optimization of the recycling rate and by selecting very narrow ranges or even constant values for the split factors. Include appropriate constraints on the input quality of the metallurgical processes.
  - Establish an optimal recycling flow sheet (from the total flow sheet) by optimizing for a maximal recycling rate, including appropriate constraints on the input quality of the metallurgical processes. Use practically well ranged split factors.
  - Monitoring/ISO norm
    - Use the results of your case studies and conclusions/findings of your modeling work to argue how a recycling system should be monitored in view of EU legislation.
    - Relate this discussion to your case study on the definition of a new or improved ISO norm.
  - AMPL (Another Mathematical Programming Language)
    - Solving an AMPL model may be done at the following address, a good on-line solver can be found: http://www-neos.mcs.anl.gov/neos/solvers/NCO:IPOPT/solver-www.html.
    - In order to get a model solved, 3 different files have to be uploaded: a model file (*.mod), a data file (*.dat) and a commands file (*.run). The first two files are required to define a model, the last one is only important to make the solver display the required output.
    - Upload the three files, click on 'Submit to NEOS'. The solver will display the solution.

Part IV

Aluminium Metallurgy and Recycling

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Chapter 11

Raw materials for aluminium production

This section gives a detailed overview of aluminium recycling with a brief introduction to primary aluminium production. Recycling of metals and materials occurs at the intersection of the Technology Cycle and the Resource Cycle as depicted by Figure 1.1. This part of the book will demonstrate the complexities that arise if this intersection is not fully understood, directly affecting the loss of material from the cycle. Understanding the depth between product design and subsequently metallurgical thermodynamics will provide the detailed knowledge to minimise losses during recycling and hence improve the environmental performance of the cycle. The light metals best represent this category, aluminium being the example used as an illustration. In order to define metrics, various levels of modelling, both theoretical and industrially orientated, will be discussed in detail. Therefore, this section on aluminium illustrates the complexity of metallurgy and makes clear if the first principle and process details are not understood it is rather risky to start talking about sustainability. In other words, the bigger cycle of aluminium cannot be described if salt flux[1] chemistry of aluminium recycling is not fully understood and how product design affects this!

11.1 Aluminium primary raw materials

The aluminium content of the earth's crust (first 30 km) is about 8 wt.%, i.e. aluminium is the most common metal in the earths crust. It is therefore necessary to explain why 39 of the 71 metallic elements (excluding radioactive elements) were discovered long before aluminium. Despite its abundance, aluminium exists in the earth crust in its oxide form only. Aluminium oxide, however, cannot be reduced by carbon to metal below 2000°C, but is instead converted into aluminium carbide. As long as our ancestors had only charcoal as a reducing agent they were only able to achieve temperatures slightly above 1000°C, a temperature sufficient to reduce and melt copper, zinc, lead, tin, silver or any alloys of it. The temperature was also sufficient to reduce iron from its oxide ores and to sinter the produced iron metal. This is the reason why aluminium metal droplets were never found in our ancestor's melting leftovers or in their cooking fire embers, even by accident. However, since then much as changed...

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[1] A molten mixture of salt is called a flux in this text, as opposed to a slag which is a molten mixture of oxidic compounds.

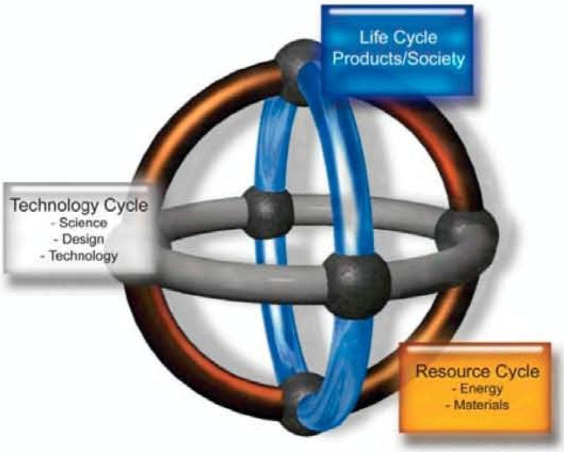

Figure 11.1: Recycling of material : The interface between the Technology Cycle and the Resource Cycle [51][52]

Davy and Oerstedt first discovered aluminium in 1824 and between 1852 and 1854 Bunsen tried to produce aluminium metal by electrolysis from alumina. The ore for primary aluminium winning is bauxite, the name originating from the little village Les Baux in southern France, the location where the first bauxite was discovered and identified. Bauxites are typical products of weathering of aluminium-silicate containing minerals, occurring often where in previous geological periods high temperatures and heavy rainfalls prevailed. According to its geological origin, 90% of bauxite mines and deposits are concentrated in the present tropical zones (western and central Africa, northern and central South America and Australia), while the European bauxite deposits (e.g. in Yugoslavia) are the result of the disintegration of limestone.

11.1.1 Ore reserves and bauxite

At present the total reserves of bauxite are estimated to be about $140 \cdot 10^9$ tons, of which about $23 \cdot 10^9$ tons are economically exploitable reserves. The world demand of bauxite is in the order of magnitude of 100 million tons/a (or tons/year) i.e. the known economic reserves are sufficient at present level of production for 230 years, however, using a 2%/a steady global growth rate these reserves are sufficient for only another 87 years of production. A rule of thumb defines the relationship between bauxite ore, alumina (alumina is pure Al_2O_3) and primary aluminium i.e. 4 t of bauxite = 2 t alumina = 1 t primary aluminium. However, in reality the alumina content varies from deposit to deposit; Table 11.1 depicts essential components (in wt.%) of important bauxite ore bodies.

The major constituents of bauxite are summarized in Table 11.1 as simple oxides, these are a mixture of different mineral components consisting of hydroxides, oxo-hydroxides and oxides of Al, Fe, Ti and Si, as well as traces of V, Cr, P, As, F, S, Ca, Mn, Cu, Zn, Be, Ga, Re and often accompanied by organic matter. Primary aluminium winning is also the main source of Gallium, which is found in bauxite at concentrations varying between 0.0025 - 0.01 wt.%. This results in a global scale production of approximately 100 g Ga/t primary aluminium metal.

Table 11.1: Compositions of important bauxite ore bodies - major constituents

Origin	Al_2O_3	Fe_2O_3	SiO_2	TiO_2
Weipa/AUS	54-56	11-13	5-6	2-3
Eleusis/GR	51	30	2	2.5
Gove/AUS	50	16-17	4	3-4
Linden/GUY	59	2-3	4	3-4
JAMAICA	49-51	19-21	0.7-1.6	2.5-2.7
Boke/GUIN	62	3-4	1	3-4
HUNGARY	50-60	1-8	15-20	2-3

Table 11.1 reveals that the alumina content of presently mined bauxite ranges from 50-60%, equivalent to 25 to 30% Al. The actual recovery of aluminium as alumina is strongly influenced by the minor constituents, i.e. at the end the average aluminium recovery from bauxites is not higher than 25%. In comparison to customary iron ores, bauxite is a rather low-grade ore. Aluminium is found in bauxite in three different mineral components: Gibbsite (α-$Al(OH)_3$), Boehmite (γ-AlOOH) and Diaspore (β-AlOOH). Gibbsite is easily soluble in NaOH, the other two minerals require higher concentrations of NaOH and temperature. The western industrialised countries, which lack bauxite deposits, tend to ignore alternatives to bauxite for economic reasons. Large reserves of domestic aluminium-silicate containing materials containing not more than 10-20 wt.% Al, such as clay, refuse slate from coal or anorthosite. Aluminium (as alumina) winning from these low grade ores is technically possible, however, presently not economically.

11.1.2 Mining

Bauxites are preponderantly mined in open pits, very rarely in underground mines. Bauxites in Europe, being a result from limestone disintegration, are frequently covered by solid rocky limestone, called overburden. This overburden could - according to an example inspected by one of the authors in Bosnia - reach a thickness of 15m situated above 1.5m of bauxite. Such an overburden to ore ratio creates very high mining costs due to the need for stoping and blasting. Due to the currently low import costs of bauxite/alumina, such mines cannot survive without questionable subsidy: Open pit mining costs in Australia are in the order of magnitude of 1 $/t bauxite, whereas the mining costs for the above mentioned Bosnian mine have been estimated at 45 $/t bauxite.

11.2 Aluminium secondary/recycled materials

Aluminium recycling is limited to metal containing material, which is called scrap (*aluminium scrap is the industrially generated equivalent to bauxite provided by nature*). Aluminium scrap is characterised by (a) the type of alloy and (b) the source of origin, with two major alloy types viz.:

- wrought alloys - $<$ 1% Si, used for rolling and extrusion , and
- cast alloys - $>$ 5% Si, used for castings.

Example 11.1

A refiner has to produce an aluminium alloy with a maximum of 150 ppm Cr. The already purchased scrap contains 200 ppm Cr. Primary aluminium (price 1450 €/t) with 1 ppm Cr and wrought alloy scrap with 20 ppm Cr (price 1200 €/t) are available. Which offers the most economic blend?

D – kg diluting metal/t scrap

Cr content of scrap: $1000 \times 0.0002 = 0.2$ *kg Cr/t scrap*

Primary Al input: $(0.2 + D \times 10^{-6})/(1000 + D) = 0.00015$

D = 336 kg; cost 487 €/t scrap

Wrought scrap: $(0.2 + D \times 20 \times 10^{-6})/(1000 + D) = 0.00015$;

D = 385 kg; cost 462 Euro/t scrap.

In this case the use of wrought alloyed scrap offers the cheapest solution.

Scrap can be generated during melting, manufacturing, fabrication or machining of products made of aluminium alloys, called prompt or new scrap, because it has not seen a customer and has not entered the use-cycle. The other source of scrap is the products manufactured from aluminium alloys after their lifetime, called old or collected scrap. Both of these categories could consist of wrought and cast alloys, some aluminium alloy scrap categories being summarized by typical examples in the Table 11.2.

Table 11.2: Examples of aluminium scrap categories

	Wrought alloys	Cast alloys, including Cu-free deoxidation alloys
New scrap	foils, window profiles, wire and sheet rejects	risers, casting rejects, turnings from castings
Old scrap	car-plates, road signs, used packaging foils, wires and cables, bottle caps, used beverage cans (UBC)	shredded cast scrap, scrap from sink-float plants, car engines

Over the last few decades trading with metals and scrap has developed its own trade practice. In addition to these trading practices, the development of scrap classifications has also facilitated the trading business significantly. Different classes of traded scrap, distinguished by code words (e.g. in Germany beginning with A for aluminium), are described according to their main physical and chemical properties. A European standard (EN) has been published (see Section 13.2.10).

11.2.1 Unalloyed scrap and residues

There is almost no important application of unalloyed pure aluminium (>99.99% Al), for it is too soft to be useful for construction purposes. The use of unalloyed primary aluminium (99.5% Al) is limited to a few sectors viz.:

- steel industry for deoxidation and alloying of cast iron and special steel sorts,
- alloying element for bronze and Cu-Al-alloys,

- fabrication of light reflectors,
- spray coating of steel products,
- painting with aluminium powder (<0.0004 mm) and special resins, and
- aluminothermic production of metals such as Mn, Mo, Cr, and W.

In these applications aluminium is irreversibly converted into products, which are excluded from any present method of aluminium recycling. Within the primary metal winning system there are only very limited sources of material accessible for recycling. The only countable source for primary aluminium recycling is the dross skimmed from transportation vessels for liquid aluminium prior to alloying, as well as holding furnaces. The metal content of dross is between 40 and 60%, the rest is alumina with traces of AlN. Usually up to 20 kg of dross/t liquid primary aluminium is generated.

11.2.2 New scrap

New or prompt scrap results from processing and machining of products made of aluminium alloys, making it a preferred scrap category since

- it does not contain the corroded surface typical of end-of-life products, and
- it's composition is quite homogeneous, for it stems in most cases from a distinct process step, a single alloy type, and from a known origin.

For these reasons the aluminium industry recycles significant tonnages of this scrap category internally, i.e. most of this scrap will not be offered to the outside. The specific statistical data are therefore widely unknown and the only tool that can be used to estimate the yearly tonnage of these internal cycles is a plausibility check with a suitable model. The yearly tonnage of new scrap has continuously grown during the past years, the reason for this being the direct link between aluminium consumption and new scrap generation i.e. the more aluminium consumed, the more new scrap generated. A rough assessment by Kammer [359] produces the following scrap generation data:

- new scrap of wrought alloys from rolling sheets 45-79%,
- new scrap of wrought alloys from extrusion 25-50% of input,
- new scrap of cast alloys from die-casting 42-60%, and
- new scrap from ingot mould casting 40-65% of input.

Cadre 11.1

The reference basis for the scrap generation data remains unclear, however, assuming 50% referred to the input, then 1 t of metal would generate 1/2 t of produced products and 1/2 t of new scrap. If the reference base were the produced products, 1 t of metal would generate 2/3 t of products and 1/3 t of new scrap. Nevertheless, whatever is meant by the data of Kammer [359], the amount of new scrap generated annually in Europe is high! What fraction is internally recycled and what is offered to external recycling remains unknown! From a second source of data [47] it can be concluded that about 40% of the feed to a rolling mill is new scrap as well as about 37% of the input to extrusion plants. However, this publication does not offer any hint how much of the new scrap/volume is offered to the outside market.

New scrap usually does not need any particular scrap processing, except compacting or cutting steps to adjust it to the local furnace charging system. Turnings from machining processes and dross are also considered to be new scrap. Cutting fluids (oils, esters, and their emulsions with water), however, usually contaminate turnings. Dross stemming from primary aluminium and semi-fabrication plants contains metals as unalloyed aluminium or wrought alloys. Frequently this dross contains fluxes of variable composition. Dross from foundries contains metal as cast aluminium alloys. Usually this dross contains sizeable amounts of nitrides (both of aluminium and magnesium) resulting from de-gassing processes in the alloying/refining furnaces. The nitrides react spontaneously with any available moisture (even air humidity) to form ammonia, which could be called the specific odour of dross.

11.2.3 Old scrap

Old or collected scrap originates from end-of-life products, implying that there is a time between production of products and generation of scrap, i.e. its lifetime. In contrast to new scrap the future generation of old scrap can be estimated and the evaluated figures compared with actual tonnages. Statistical data are available for aluminium consumed by various end-use sectors. Their average lifetime, collection rates and metallurgical yield lead to data, which can be compared with actual data. The yearly tonnage of old scrap has also continuously increased during the past, which is more a result of collecting, sorting and melting endeavours than of previous machining techniques. Old scrap is unavoidably corroded, often coated by plastic or paints, contaminated by inserts of metallic and non-metallic character (e.g. an car engine contains inserts of (stainless) steel, copper, is partly coated by sealing material, etc.). Due to these specific properties old scrap usually requires extensive scrap processing i.e. liberation of particles by shredding, sorting of particles by hand or multi-components sensor systems, separation of particles by density differences (sink-float), magnetic separation, eddy-current, etc. Due to the widespread mixture of wrought and cast aluminium alloys, the alloying elements in old scrap could possibly reach the maximum contents shown in Table 11.3 [360].

Table 11.3: Possible maximum concentrations of alloying elements in old scrap

Alloying element	Maximum concentration (%)
Chromium	1.5
Copper	4.0
Iron	2.5
Manganese	1.0
Magnesium	4.0
Silicon	14.0
Titanium	0.12
Zink	3.3

A comparison between the frequently produced aluminium alloy AlSi9Cu3 and a typical average composition of shredded old scrap depicted in Table 11.4 supports this statement (note that scrap composition can change with time as a function of product design). If old shredded scrap is processed in sink-float plants using haematite or FeSi as a heavy medium, the critical iron content in aluminium can under certain circumstances be further decreased in the aluminium scrap using this technique, however, poor removal of the FeSi from the aluminium concentrate could also lead to the opposite effect.

Table 11.4: A typical comparison between the composition (in mass %) of AlSi9Cu3 and shredded old scrap (note that this compostion changes with time!)

	Shredded old scrap	AlSi9Cu3
Cu	1.5-2.0	2.0-3.5
Fe	1.0-1.5	<0.8
Si	4.0-8.0	7.5-9.5
Zn	0.8-1.2	<1.2
Mn	0.4	0.15-0.65
Mg	0.3	<0.55

Cast alloy scrap

According to 2001 data from the EAA (European Aluminium Association, Brussels) the fabrication of cast aluminium alloys in Europe reached 2.09 million tons/a. Including another 97000 t of imported cast material implies that the market absorbed 2.187 million tons cast alloys/a in total. This tonnage is the source of the future old collected cast alloy scrap, generated in two categories viz.:

- during fabrication = prompt scrap, e.g. turnings, dross, rejects, and
- products made from cast aluminium after having passed its lifetime = old scrap, e.g. collected scrap from shredders, sink-float plants.

One essential objective of foundries is to increase the precision of castings. The consequence would be a decrease of the specific generation of turnings during machining in kg turnings/t good cast, or at least a shift of the average size of turnings to the smaller prticle size fractions. Both would have a particular influence on the recovery of metal from that type of scrap. The order of magnitude of turnings that are generated per ton of good cast (a significant variance of the 100 kg is expected to exist) is approximately 100 kg. Cast alloy scrap is the prevailing feed of refiners, which are aluminium smelters that buy all kinds of collected old and new scrap and produce standardised aluminium cast alloys from them. Remelters usually re-melt clean scrap of one distinct alloy type into ingots, slabs or billets. Usually the scrap belongs to the customers that pay the remelters a melting charge on the basis of a mutually agreed melting yield . Due to the increasing tendency of excellent scrap sorting, remelters absorb more and more clean cast scrap in competition with refiners.

Wrought scrap

In Europe in 2001 the fabrication of semi-products consumed 6.555 million tons of wrought alloys, of which about 15% originated from recycling of previously produced wrought alloy products. From this input all semis manufacturers produced 6.266 million tons of new wrought alloy products, i.e. the metal yield was 95.6%! The rolling branch absorbed 3.344 million tons, the extrusion sector 2.422 million tons and the rest into various other products. The extrusion branch produces products like frames for windows and doors (predominantly for non-residential buildings), construction profiles in buildings, airplanes, railroad cars and automobiles. Typical rolled products are beverage cans, sheets for facades on buildings, car bodies, airplanes and railroad cars, foils for packaging purposes, etc. Depending upon the average life-time of these different sectors (*which is short for beverage cans and packaging material and* *long for construction material in transportation systems, and very long for buildings*) the recycled tonnage is more or less closely related to the present production. Due to the multitude of products, their specific lifetime distribution (which is mostly a skew distribution curve), growth rate etc., there are hardly any convincing mathematical models available to accurately predict the tonnage to be expected for any year to come. Nevertheless, a few considerations lead to some special cases. The major part of all foils used by the packaging sector is lost to recycling: the extremely thin thickness and the combination with plastic foils or other foreign material (resins from colours) makes foils an economically unattractive or expensive recycling material. Thin foils also need extreme amounts of flux (a molten salt mixture), irrespective of any preceding compacting step, and the metallurgical yield is rather disappointing. Used beverage cans (UBC) are recycled in different countries in Europe, sometimes with high collection rates (Switzerland >85%). However, a large country like Germany packages only 15% of its drinks into aluminium cans. 85% are bottled in a three-metal containing can: tinned steel with an aluminium lid. The questionable recycling of these luxurious cans in Germany has thrown a shade of doubt on the recycling of UBC there. Not in vain did the German government try to enforce the recycling of UBC by law. Since UBC represent, with regard to composition, a rather homogeneous scrap they can be re-melted and cast into slabs. UBC are a remarkable exception of the rule that old collected scrap is used for the production of cast aluminium alloys only. Bottle caps for example are returned to the use-cycle at a rate of approximately 90%. Wrought alloys are customarily sought by remelters, however, due to the refiner's constant need of low alloyed aluminium for dilution of troubling constituents in scrap the amount of wrought alloy in a typical refiner scrap yard is always impressive.

Chapter 12

Pre-treatment of aluminium containing material

Physical separation is the first step in the separation of inert or gangue material from an ore or metal from an end-of-life product. Typical grade-recovery curves visualize mathematical models describing such physical separation functions, which are specific for each ore or scrap. Besides separating metal from gangue, different metals also need to be separated from each other. In primary metal winning the separation of gangue from ores leads to so-called concentrates. In the recycling branch the separation of inert material from scrap and the separation of different metals from each other are similarly important, to concentrate the metals.

12.1 Mineral processing of aluminium ores

Bauxite, regardless of whether their origins are from the disintegration of laterite or limestone, being oxy-silicates of which lattice aluminium-atoms are part. Classical mineral ore beneficiation (include milling and flotation) would therefore not result in any up-grading of aluminium; it would just produce two fractions with more or less identical aluminium contents. The only separation happens directly in the open-pit mine, when barren overburden is separately excavated and used as future back-fill material in the mine or for landscaping.

12.2 Separation processes for aluminium metal containing material

Aluminium scrap contains foreign metals (of which some are typical alloying elements) and non-metallic components (inorganic or organic). The aim of recycling aluminium scrap is to achieve a maximum metal yield in the later melting process. Metal yield has been described in Chapter 10, illustrated by the following example to refresh the idea.

Example 12.1
1 t of collected mixed aluminium scrap taken from a demolished building contains 10% foreign metals and 10% non-metallic components. Foreign metals may be partly inserts, the non-metallic components may be represented by fixed or loosely adhering coatings. Without any further processing the metallurgical yield of this ton shall be 70%. Alternatively the

non-metallic components were separated by 90%, however, 3% of the original aluminium content is lost therein. Subsequently 95% of the foreign metals were separated, however, also in this step another 2% of the original aluminium content is lost with the separated metals. As a result of these separation processes the previous ton of scrap is reduced to only 775 kg scrap, however, the aluminium content increased drastically from 80 to 98%. The metallurgical yield of this pre-processed scrap is now 93%. In the first case 1000 × 0.7 = 700 kg, in the second case 775 × 0.93 = 721 kg of aluminium alloy is produced per t of untreated scrap. In this particular example scrap processing resulted in a higher metal yield.

Any scrap processing should not only improve the aluminium or metal grade, but also make scrap ideal for handling and less prone to oxidation. A very meaningful parameter to measure oxidative loss is the specific surface ($S_{surface}$) of scrap particles *(i.e. the surface area in mm^2/g or m^2/t)*. The base format of a block can be used to calculate the specific surface of any profile, sheet, foil, turning, or even shredded cast particle, while the format of a spherical ball is applicable to the calculation of the specific surface of dross and salt flux granules. All particles are covered by an oxide layer of variable thickness and since the densities of both the oxide and metal are known, the specific surface is easily calculated by the following:

Blocks

$$\text{Particle volume} \quad V_p = L \times W \times H \quad (m^3) \tag{12.1}$$

$$\text{Particle surface} \quad S_p = 2 \times (L \times W + L \times H + W \times H) \quad (m^2) \tag{12.2}$$

$$\text{Metal volume} \quad V_m = (L - 2d) \times (W - 2d) \times (H - 2d) \quad (m^3) \tag{12.3}$$

$$\text{Oxide volume} \quad V_o = V_p - V_m \quad (m^3) \tag{12.4}$$

$$\text{Mass metal} \quad M_m = V_m \times \gamma_m \quad (t) \tag{12.5}$$

$$\text{Mass oxide} \quad M_o = V_o \times \gamma_o \quad (t) \tag{12.6}$$

$$\text{Mass particle} \quad M_p = M_m + M_o \quad (t) \tag{12.7}$$

$$\text{Specific surface} \quad S_{surface} = \frac{S_p}{M_p} \quad \left(\frac{m^2}{t}\right) \tag{12.8}$$

Spherical balls

$$\text{Particle volume} \quad V_p = \frac{4}{3}\pi r^3 \quad (m^3) \tag{12.9}$$

$$\text{Particle surface} \quad S_p = 4\pi r^2 \quad (m^2) \tag{12.10}$$

$$\text{Volume metal} \quad V_m = \frac{4}{3}\pi(r - d)^3 \quad (m^3) \tag{12.11}$$

$$\text{Oxide volume} \quad V_o = V_p - V_m \quad (m^3) \tag{12.12}$$

$$\text{Mass metal} \quad M_m = V_m \times \gamma_m \quad (t) \tag{12.13}$$

$$\text{Mass oxide} \quad M_o = V_o \times \gamma_o \quad (t) \tag{12.14}$$

$$\text{Mass particle} \quad M_p = M_m + M_o \quad (t) \tag{12.15}$$

$$\text{Specific surface} \quad S_{surface} = \frac{S_p}{M_p} \quad \left(\frac{m^2}{t}\right) \tag{12.16}$$

where:

L = length of block (m)
W = width of block (m)

H	= height of block	(m)
d	= thickness of oxide layer	(m)
r	= radius of ball	(m)
ρ_m	= density of solid metal (=2.75)	$\left(\frac{t}{m^3}\right)$
ρ_o	= density of oxide	$\left(\frac{t}{m^3}\right)$

Oxide layers have the following thickness:

- Natural oxidation on air: $< 0.1\mu m$
- Artificial chromating/phosphating: 1-$3\mu m$
- Anodic oxidation: 2-$20\mu m$
- Hard anodizing: 15-$30\mu m$

Since the values for specific surface range between 10 and 100000, it is convenient to use logarithmic values i.e. $\ln(S_surface)$. For any particle the theoretical metal and oxide content can be calculated, the data entered into a mass balance of a sampling furnace and the metal yield compared with the theoretical metal content. By the variation of the basically unknown thickness of the oxide layer the balance shall be closed. In Table 12.1 typical specific area ranges for different scrap categories are listed.

Table 12.1: Typical specific surface ranges mm^2/g for different scrap categories

Scrap category	$\ln(S_surface)$
Turnings	6.77-7.7
Bottle caps	7.3
Sheet	5.53-6.63
Foil	8.93-9.22
Ingots	2.12-2.6
Cast shredded	3.2-5.4
Chips	6.0-6.7
UBC unshredded	8.93
Salt flux granules	4.7-6.7
Wire	4.33-5.93
Dross granules	2.6-7.2

12.2.1 Separation methods for aluminium recycling

In this section a very brief description of techniques used for the processing of aluminium alloy containing materials is given (also used to separate other end-of-life materials & products). These processes are required due to the differences of scrap regarding size, shape, particle size distribution, contaminations by non metals and foreign metals, etc., most of which occurred during the use phase of aluminium made products. Table 12.2 shows a classification of scrap based on practical experience by scrap yards in addition to computer modelling *("$++$" → "important" to "$-$" → "no effect")*. The separation processes for metal containing material is highly dependent on the requirements of the subsequent metallurgical winning process. Those metals that are reducible with carbon near their melting temperature have in principle the same process for primary and secondary raw materials (copper, lead, zinc, iron, precious metals). It is irrelevant whether secondary raw material contains the metal in metallic state or as a chemical compound. For a small group of metals the process route for primary raw materials differs entirely from that for secondary raw materials (e.g. aluminium, magnesium). Figures 12.1 and 12.2 demonstrate the necessity for aluminium scrap to be protected against oxidation during its whole utilization and processing cycle.

Metal : non-metal separation

- Manual separation of non-metals on sorting belts from collected scrap
- Crushing and screening of dross
- Separation of turning fines by screening
- Air classifying after treatment of cables and wires with liquid nitrogen
- Air separation of fluff after shredders
- Separation of non-metals by sink-float systems
- Eddy-current separation of non-metals from collected scrap
- Magnus rotors for separation of plastic from wires and cables, or flux constituents from metal granules in bottom ashes from incineration plants

Light metal : heavy metal separation

- Manual separation on sorting belts from coarse collected scrap
- Automatic sorting by laser or X-ray sensors or its combinations applied to mixtures of rather fine scrap fractions
- Separation of stainless steel, copper, zinc, and lead alloys from aluminium and magnesium alloys in sink-float plants
- Magnetic separation of iron- and steel particles from any kind of aluminium containing scrap
- Eddy-current separation of copper- and zinc-alloys and stainless steel from fine fractions of already processed aluminium scrap

Light metal : light metal separation as was as aluminium alloys

- Manual separation on sorting belts of alloys with colour coding, or on basis of visible fracture appearance
- Separation of magnesium alloys from aluminium alloys by sink-float plants
- Automatic sorting by laser or X-ray identification of already processed aluminium scrap
- Screening after high temperature crushing, e.g. for UBC or separation of wrought from cast alloys.

Table 12.2: Aluminium scrap categories

Scrap category	Examples	Surface to mass ratio (m^2)	Surface contaminants					
			no	organic	inorganic			
				loss of ignition	oxide, sand	flux, salt	foreign metals	
							Fe, SS	Si, Cu, Ni, Mn, Mg
I	foil, sheets (plastic & paint coated), bottle caps	>1000	-	+++	-	-	-	-
II	clean profiles, billet ends	<1000	+	-	-	-	-	-
III	swarf, chips, turnings	1000-5000	-	+	+	-	+	-
IV	shredded parts from sink-float plants	100-1000	-	++	++	-	+	+
V	pretreated dross, flux granules	100-5000	-	-	++	+	-	+
VI	untreated dross	100-1000	-	-	+++	+	+	+

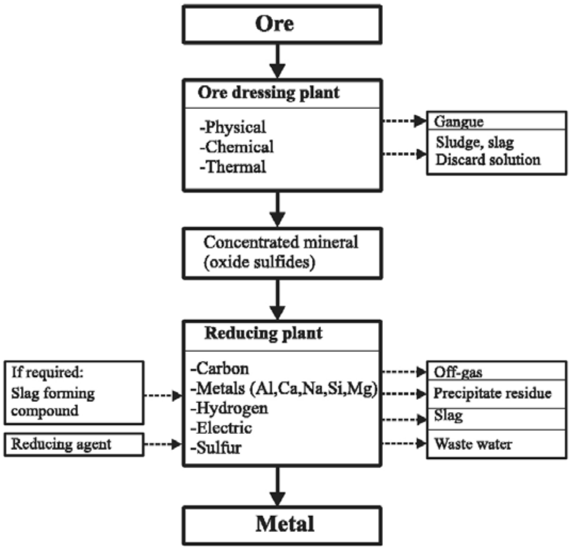

Figure 12.1: Principal scheme of primary metal winning

Cadre 12.1

The importance of cutting and sorting techniques is impressively documented by statistical data from North America [361]. In the year 2000 there were roughly 3000 scrap collectors and car dismantlers, approximately 200 shredders, 12 sink-float plants and 1 heavy metal sorting plant. Fascinatingly the average ratio from step to step is about 15:1, i.e. 1 heavy metal sorting plant/15 sink-float plants, 1 sink-float plant/15 shredders and 1 shredder/15 scrap collectors. On one hand the figures reflect the decrease of mass from e.g. a car to the heavy metal fraction, but on the other hand the increase of added value. For example the value of a car wreck is zero if not negative, due to disposal costs. After shredding, magnetic separation and sorting out the aluminium content, the value of the segregated scrap is about 700 kg steel scrap/car × 100 €/t plus 100 kg aluminium scrap/car × 1000 €/t = 170 €/car, i.e. scrap processing generated an added value of at least 170 €/old car.

Figure 12.3 depicts the contemporary treatment of old, i.e. de-registered cars. Aluminium metal that is already available in cars is of immense importance to the aluminium recycling business. The 187 million cars registered in the EU countries contain more than 10 million tons of aluminium alloys, i.e. the yearly 14-15 million de-registered cars in the EU represent an aluminium scrap potential of well above 1 million tons of metal/a. Directly after eddy-current separation, a light metal concentrate is available, to which further physical separation and automatic sorting technologies can be applied.

An aluminium intensive vehicle contains much more aluminium alloy than any average modern car. A typical example is the Audi A8, the composition of which is shown in Table 12.3 (data from Audi). The distribution of aluminium in the various components of the A8 is shown in Table 12.4. The A8 contains 34 wt.% aluminium alloy, of which 301 kg (19.7 wt.%) is cast and 219 kg (14.3 wt.%) wrought alloys.

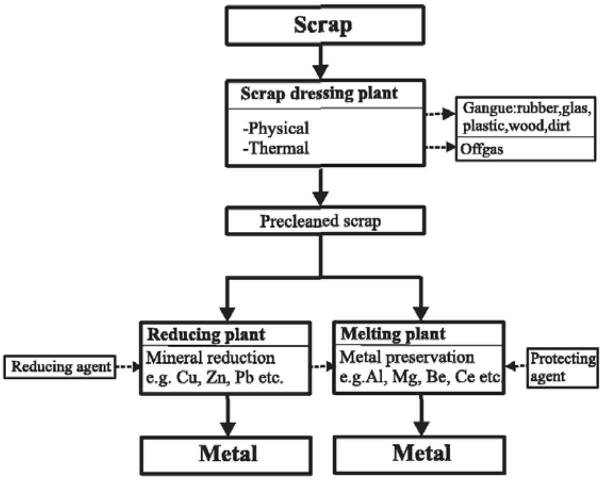

Figure 12.2: Principal scheme of secondary metal winning

Table 12.3: Composition of Audi A8 (dry mass in kg)

Aluminium	521
Iron and steel	535
Lead, copper and zinc	60
Plastic	242
Rubber	90
Glass	41
Bitumen	20
Other material	24
Total	1533

Table 12.4: Aluminium distribution in the Audi A8 (dry mass in kg)

Engine, gear box, etc. (cast)		243
Car body		
Sheet	150	
Profiles	70	
Cast joints	58	278
Total		521

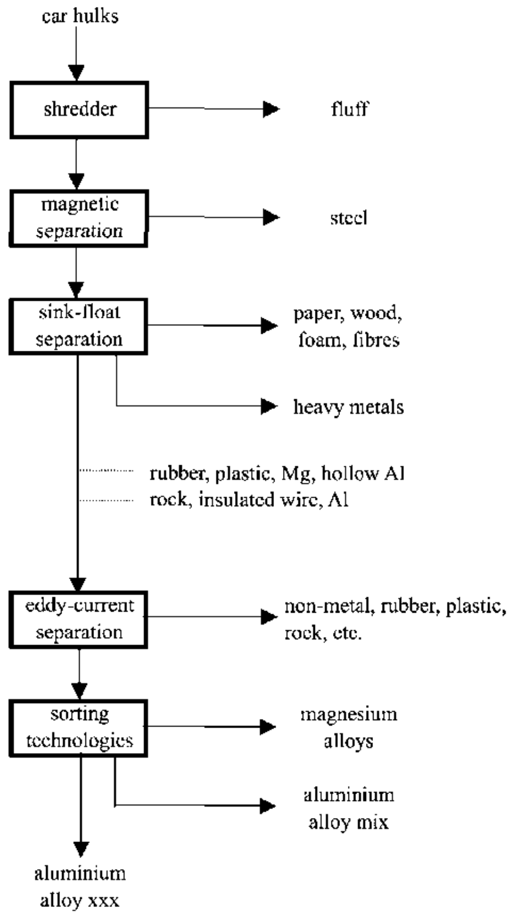

Figure 12.3: An example of the treatment of ELV's

Example 12.2

Mechanically cooled dross containing 59% metal is screened at 1mm. The fraction >1mm weighed 850 kg and contained 63% metal. The resulting metal recovery was 90%. Consequently the fine dust fraction of 150 kg contained the remaining metal, resulting in a metal content of 36%, too low a content to be economically recoverable. If the screening was carried out at 1.5 mm, the metal content of the coarser fraction was elevated to 70%, which gives much prospect for high melting yield. However, the separated mass went down to 700 kg, resulting in a decreased recovery of 83%, but the fines fraction of 300 kg contains now 33% metal.

Only a careful economic analysis of the dross processing including the subsequent melting under salt and the disposal or further processing of the fines will give an indication of the most recommendable process.

12.2.2 Shredding and cutting

Aluminium scrap can contain extremely large components, which has to be cut or shreddered into smaller pieces prior to any further treatment (see Chapter 9). There are two possible methods (i) dismantling of components into smaller pieces with only little mechanical destruction of individual components, or (ii) crushing components into smaller pieces by applying strong mechanical forces resulting in an almost complete destruction of individual components. The objective of shredding is twofold:

- liberation of individual components/elements contained in the aluminium scrap as a basis for subsequent sorting,
- size reduction for physical sepration, and
- generation of small scrap suitable for fast charging into melting furnaces.

Brittle cast aluminium alloys and dross are customarily crushed without significant deformation, whereas wrought alloys are predominantly cut resulting in a visible plastic deformation. When being exposed to high temperatures ductile wrought alloys may suddenly show fragile behaviour. If liberation of metallic aluminium components is the main objective, the equipment should generate fractures at the aluminium-foreign metal interface or the aluminium-non-metallic component interface, if possible. Without going into engineering details Table 12.5 summarizes the most frequently used crushing equipment for brittle cast (shredding) and ductile wrought aluminium alloy scrap (cutting) [360].

For large sheets a hydraulic press and a guillotine shear are combined in one machine: The press first compacts the loose sheets into heavy packages that are subsequently cut into pieces, which are ideal for charging. Shredders are particularly used to cut flattened car hulks into fist-sized pieces and to liberate individual metals (see Chapters 9 and 10). Modern automobiles presently contain about 10 wt.% aluminium alloys, which could reach 35 wt.% in so-called aluminium intensive vehicles (AIV). Such AIV contain significantly more wrought than cast aluminium alloys (car body). Without efficient sorting the wrought aluminium alloys are lost in cast alloys, since the average Si-content of the resulting alloy mix would always be well above 1 wt.% Si, as Table 12.6 depicts (Si-contents are 9.5 wt.% in cast and 0.5 wt.% in wrought alloys). Therefore only by combining shredding and sorting added value is generated over the complete material chain. The necessity of combining liberation by cutting and subsequent efficient sorting will grow as international car associations forecast an ongoing increase of aluminium consumption in automobiles in future.

Table 12.5: Most frequently used crushing equipment for brittle cast (shredding) and ductile wrought aluminium alloy scrap [360]

Scrap type	Crushing/cutting machine
Brittle scrap	
Cast scrap	hammer, impact or impeller crusher
Scrap after cryogenic treatment	hammer or impact crusher
Dross	ball, rod, impact or cage mills
Ductile scrap	
Thick-walled scrap	alligator or guillotine shears
Thin-walled scrap	hammer, impeller or rolling crusher rotary shears and shredders
Cables	guillotine or alligator shears, rotating shears
Turnings, chips	impeller or hammer crusher rotary shears and shredders

Table 12.6: Si-content of blended wrought and cast alloys

Ratio wrought:cast	average % Si
1:5	8.0
1:1	5.0
2:1	3.5
5:1	2.0
10:1	1.3

12.2.3 Processing by dry separation

Electro-magnetic separation

Magnetic separation is based on the generation of magnetic forces on the particles to be separated, which are higher than opposing forces like gravity or centrifugal force. This principle is used to separate ferromagnetic particles from crushed scrap mixtures. Magnetic separation is customarily an integrated part of any shredder plants. Type and localisation of magnetic separators (prevailingly consisting of NdFeB magnets) inside a scrap processing plant is dependent upon the type of scrap, particle size distribution of the scrap mix, throughput (t/h); and the fraction, particle size and form of ferromagnetic particles in the scrap.

Eddy current

A particular form of magnetic separation is eddy-current separation. An alternating magnetic field induces electrical eddy currents on a metal particle. This results in a magnetic field whose direction is opposite to the primary magnetic field. The exchange interactions between the magnetic fields result in a repulsive force on the metallic particle; in fact the net effect is a forward thrust as well as torque (the latter spin-effect is caused by a particular rotating magnet system, called the Magnus-rotor). This force is a function of the magnetic flux, or indirectly of the electrical conductivity and density and the size and shape of the metallic particles. Eddy-current separation is applied to aluminium containing packaging material, light and heavy metal scrap from shredded old cars and spent foundry sand from aluminium cast houses. It is vitally important that any ferromagnetic particles have been separated prior to eddy-current separation. Small (<2 mm), long and narrow particles such as wires cannot be separated by eddy-current separation.

Air classifier

For aluminium scrap separation the most important air-based sorting technique is air separation, using air classifying to separate light material like plastic, wood, paper, glass fines, etc. By combining several stages, e.g. zigzag air classifier, sufficient selectivity is achieved. The most prominent application of the air classification is in shredder plants, producing the shredder light fraction (automobile shredder residue - ASR) or fluff.

Fluidized bed separation

A fluidised bed of dry sand is used to separate aluminium particles from other materials. This technology is in principle a dry sink-float separation, which is still hampered by several difficulties: Tubular or hollow particles are filled with sand and consequently tend to sink; sand of high density is used and therefore high velocity air is needed, both tend to form unsteady currents that reduce the selectivity of separation. Nonetheless this technology is used for shredded UBC, using alumina as separation media; this fluidised bed is heated up for simultaneous decoating and combustion of organic material. It could be applied to a wide range of shredded scrap with paints and organic coatings or adhesives.

Dross processing

A particular form of dry processing of aluminium scrap is the handling of dross, which is generated on the surface of liquid aluminium in contact with oxygen-containing gasses, like air. Hot dross from an aluminium bath is skimmed into steel boxes where it is unavoidably

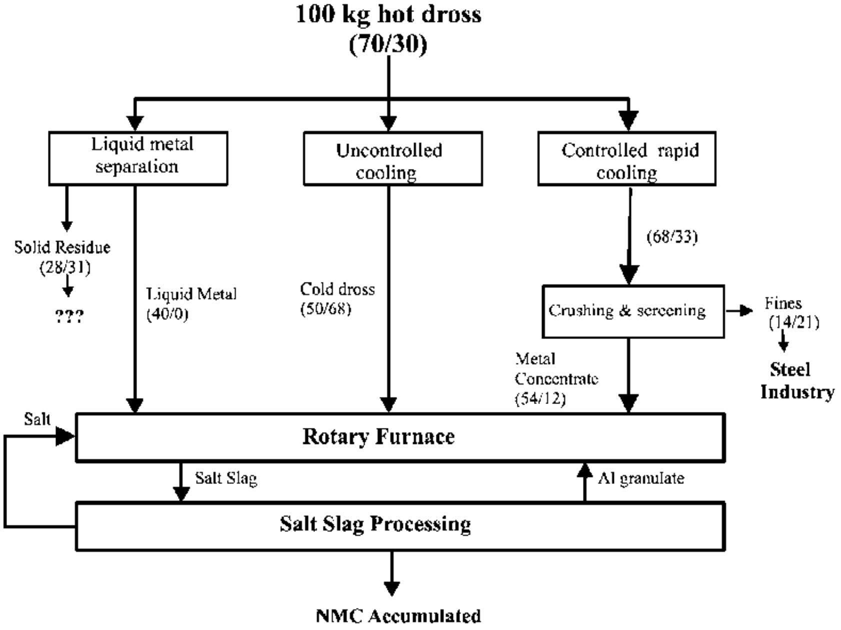

Figure 12.4: Dry dross processing for metal preservation: data given in (kg metal/kg oxides) as a typical example

exposed to ambient air and is rapidly oxidised. This oxidation process is exothermic and generates large amounts of heat. The rate of the oxidation reaction increases rapidly with rising temperature, i.e. dross burning is a self sustaining process, which comes to an end only once most of the metal is converted into the heat insulating oxide that inhibits further heat transfer. Without any intervention hot dross could burn down to a residual metal content of less than 30%, which is far below the economic break-even point for dross processing. A metal content of 40%, in lumpy pieces, may still be economically viable for separation, but a 50% metal content in particles of < 0.5 mm is certainly not. There are two principal methods available to prevent metal losses by dross burning:

- rapid cooling of hot dross to below 400°C freezes the metal and prevents it from burning; below 400 °C the oxidation rate of solid aluminium alloys is too low to be significant, and
- pressing, centrifuging, shaking or stirring of hot dross to separate as much of the entrapped liquid metal prior to freezing.

In order for any method of hot dross treatment to be properly evaluated a system analysis has to be carried out considering the mass flow and economics of the whole cycle "dross skimmed - hot dross treated - intermediate product handling and melting - internal dross and salt flux processing - granulate melting". Figure 12.4 summarizes the processing routes to be evaluated.

Cadre 12.2

Rapid cooling is carried out in water-cooled or inert gas containing rotary cooling drums. In the past a simple practise prevailed, this involved spreading out the hot dross on the smelter floor right after skimming, however, this practice proved ineffective, due to losses by ongoing oxidation and fugitive emissions. Hot dross boxes can be placed under a cover, which is filled with inert gas or evacuated, which is, however, costly and time consuming solution. Direct recovery of liquid metal is very effective. Stirring or centrifuging needs moving machine parts at high temperature under corrosive atmosphere, which make them susceptible to malfunction, therefore low availability and high repair/maintenance costs are often the consequence. Dross presses allow a recovery of up to 60% of the entrapped liquid metal. Zahorka [362] claims 20-30% metal, others mention up to 50% metal [359]. An accurate calculation, however, must include the treatment cost of the depleted dross cake, which could be huge in size, in the solid phase, but low in metal. Hot dross treatment will be described in detail in Chapter 13.2. Once dross is cooled down the downstream process for dross treatment are rather clear: Liberation and separation of entrapped frozen metal and controlled outlet of the accumulated oxide mixture. Cold dross can be considered as a 2 or 3 component material: metal, oxide, or rather called ***N****on-****M****etallic* ***C****omponents (NMC), and flux. Dross consists of entrapped metal and metal converted to oxides, both of which were previously purchased, i.e. money was paid for them. Eventually the oxide in dross has to be separated from metal by the addition of salt, thus generating salt flux, which carries away re-entrapped metal. Although the salt flux is processed in Europe and about 80% of the entrapped metal is separated, it has to be repurchased by the previous owner, the secondary smelter. Dross is the main intermediate product in which NMC, generated during the usage cycle of aluminium alloys, are accumulated. The most important factor in the economics of aluminium recycling is the recovery of aluminium metal. In order to understand the whole aluminium cycle the outlet of collected NMC via dross is of crucial importance. In principle milling and screening of cold dross is a classical mechanical process to generate metal concentrates by separating gangue. During dross treatment metal droplets are liberated from the surrounding oxide matrix by milling. Ball, rod or cage mills are customarily used. Screening separates coarse metal granules from barren oxide fines. In practice the oxides are never free of metal and the whole process is a compromise between recovery of coarse metal fraction and the amount of generated dust. A rather new process for cold dross has been recently developed in the USA. In a so-called tumbler the dross is actually squashed rather than crushed. The brittle oxides split from the more ductile aluminium metal particles and a high recovery as well as a high metal content in the different fractions is reported [359]. The further treatment of the high NMC, low metal fraction is of critical importance. The fines separated from cold dross contain still 10 to 15 wt.% metallic particles. The low metal content and the extreme fineness made any kind of pyrometallurgical recovery of the metal impossible. In the 80's this dross dust - then called "ball mill dust" - was co-processed with salt flux. Since then this dust has been used by the steel industry for deoxidation and other thermal applications.*

Image processing

During handpicking people identify different metals by visual cognition of different colours (red copper, yellow brass). A first step in automation is the development of colour-sorting technologies, which sense the colour of each particle and then use computer control to mechanically divert particles of identical colour out of the product stream. Since each particle has to be separated, the throughput of such a sorter is particle-size dependent. Such colour sorting techniques have been in operation for more than 10 years, and have been used for the separation of zinc, copper, brass and stainless steel with product purities of >98% each [361]. If the main objective is to separate aluminium alloy particles from shredded non-ferrous metal fractions and up-grade it with high recovery, then colour sorting alone would be inefficient. This is because aluminium alloys are partially painted (in particular from aluminium intensive vehicles, automobiles with >35% Al) and because most other metals also appear greyish. It is therefore difficult to separate Al and Mg based only on colour, although selective etching by spraying NaOH or HNO_3 on particles increase the colour differences between the metals. This reveals a fundamental problem of particle separation: Shredding of post-consumer products results in mixtures of particles that show a distribution in composition, size, shape, texture, types of inserts, coatings, etc. The variance of these different particle properties complicates identification that is solely based on a single principle [363]. For this reason the combination of different identification methods and mechanical sorting techniques is the most promising and applied route to achieve an efficient up-grading of aluminium alloys with a high recovery.

X-ray sorting Dual energy X-ray transmission imaging, well known and practised for luggage safety inspections at airports, is a fascinating method of particle identification [363]. This technique identifies particles based on the average atomic number, particle shape, internal structure (e.g. characteristic variations of thickness) and presence of characteristic insert material. This X-ray system is fortunately rather insensitive to particle thickness and surface contaminations. Aluminium cast alloys and magnesium die-cast alloys can be identified and sorted based on their characteristic alloying elements. It is possible that typical differences in shape could soon also be used to distinguish between cast and wrought light metal alloys. A combination of eddy-current detection and dual energy X-ray transmission imaging is particularly promising in this respect.

Laser-Induced Breakdown Spectroscopy (LIBS) sorting Another identification method is the laser-induced breakdown spectroscopy (LIBS). This method was initiated by Los Alamos National Laboratory/USA and Metallgesellschaft/Germany about 20 years ago. In the meantime Huron Valley Steel Corporation/USA developed a commercial scale sorting system based on this technology [361]. Wrought and cast aluminium alloy scrap concentrates are lined up on a conveyor belt where a vision system locates and targets individual particles. A series of focused ablation laser pulses are delivered to the same spot on each particle. A pulse of an ablation laser vaporizes only the first nanometers of the surface i.e. the first pulses are necessary to clean the surface of oxide layers, which have a different composition than the mother metal. The last pulse vaporizes a tiny amount of metal generating a highly luminescent plasma plume. The light from the plasma is collected and analysed by an industry standard optical emission spectroscopic method to quantitatively determine the chemical composition of this part of the surface. This composition determines to which product bin the particle is directed. This non-contact method is reported to be used now in a commercial scale sorting plant for about 45 000 t aluminium particles/a. Foreign metals are diverted from the aluminium product stream and cast and wrought aluminium alloys are separated. Recent development is reported on new electromagnetic sensors using a pulse magnetic field [364]. The future prospects of this system are mesmerizing, in particular with respect to cost and simplicity. Combining the above mentioned individual sensors with integrated data processing will in future be the preferred technique to up-grade aluminium alloy families with high purity and recovery (also see Figure 4.8).

12.2.4 Processing by wet separation

Densities (t/m^3) of non-metallic components and most metals differ significantly, as is shown in Table 12.7. Separating materials by using the difference in their density has a long history.

Sink-float

The sink-float method is of importance to concentrating aluminium scrap. A heavy medium, consisting of a suspension of fine haematite or FeSi in water, separates high density particles (that sink to the bottom) from light material, that floats on the surface of the suspension. FeSi (with a density of 6.7 t/m^3) is ground to a particle size small enough to keep it suspended in water. In the first stage the pulp density is adjusted to 2.2-2.5 t/m^3 (volumetric pulp density of 21-26 vol.% FeSi), in which wood, paper, plastic and magnesium alloys are separated [360]. In the second stage the density of the pulp is adjusted to 2.9-3.4 t/m^3 (equivalent to 33-42 vol.% of FeSi), where aluminium alloys are separated. All heavier metals remain in the sink fraction. The regeneration of the slurry is easy as FeSi is ferromagnetic. A disadvantage of this process is the unavoidable loss of FeSi with the scrap, which is in the order of magnitude of 10 kg FeSi/t scrap. This results in slightly increased iron content in the aluminium scrap. Any inclusion of heavy medium within cavities of scrap particles could carry light metals into the heavy fraction; in the second stage hollow aluminium particles e.g. from wrapped foils are unfortunately carried with the magnesium fraction. Both of the above mentioned phenomena lead to noticeable losses of aluminium in sink-float plants.

Table 12.7: Densities (t/m^3) of non-metallic components and metals

Dry wood	< 1
Rubber	0.7-1.2
Plastic	1.3-2.2
Magnesium alloys	1.7-1.9
Aluminium alloys	2.7-2.9
Zinc alloys	6.6-7.1
Steel, iron	7.7-7.9
Copper alloys	8.2-9

Heavy medium cyclones

For small aluminium scrap particles (typically from shredders: 0.5-50 mm) heavy medium cyclones are applied, where centrifugal forces are used to separate materials with different densities. The automobile manufacturing industry is continuously searching for lighter construction materials. A recent development is the combined casting of aluminium and magnesium alloys. One of the new scrap fractions from machining such combined castings are mixed turnings of both metals. Any direct melting of such mixtures (after drying the turnings) will result in an alloy, which is useless for either alloy family. Due to the differing composition of the turnings it is also extremely difficult to produce a standardized master alloy.

Jigging

A special form of jigging including a permanent specially sized bed of balls (called the ragging) could separate these mixed turnings and has proved to be a promising technology. However, special care must be taken when selecting the jigging medium, as any water-based medium will result in a rapid and spontaneous chemical reaction with the magnesium alloy, generating hydrogen and traces of precarious PH_3 gas. The separated turnings are dried, compacted and re-melted.

Cadre 12.3

Aluminium turnings from machining castings contain up to 20 wt.% cutting fluids, a mixture of different organic liquids and water. Woolly turnings are crushed and combined with fine turnings and centrifuged to reduce the total moisture content to about 4%. The separated cutting fluid is processed to regain the cutting oils, esters and water. The turnings are washed counter-currently in a warm alkaline leach (pH 9-10. temp 85° C). The turnings are then centrifuged again down to 4% moisture and conventionally processed. The spent washing leach contains various surface active agents and needs extensive pretreatment prior to being returned to the washing drum. Heat exchange, solid-liquid separation and separation of the different organic substances make this process expensive. The thermal processing of wet turnings is therefore the state of the art (see Section 12.2.6).

12.2.5 Compacting of aluminium scrap

The oxidation rate of aluminium increases with rising temperature and the oxidation of aluminium particles occurs on their surface. The oxidation is an exothermic chemical reaction, i.e. it generates heat, which increases the temperature and thus further accelerates the oxidation rate. The rate of oxidation can be expressed in kg oxidised metal/h × m^2. If it is assumed that thin-walled aluminium scrap, like foils, chips and turnings, are charged into a hot melting furnace at a temperature of 800°C, and that the time of exposure to flue-gas until such particles are covered by salt is statistically constant, then the only variable left influencing the oxidation rate is the surface of the charged scrap. For example 1 m^2 of a foil of (usually 6 - 50 mm) 25 mm thickness has a surface of 2 m^2 and a mass of 68 g. *The specific surface is therefore 30 000 m^2/t of foil! Chips of 100 mm length. 2mm width and a thickness of 0.5 mm have a specific surface of 1900 m^2/t of chips.* It is conceivable that for the preservation of such metallic scrap types reduction of the surface area is a prerequisite, therefore these materials are usually compacted by squeezing/pressing, baling or briquetting. Baled scrap has a lower density than briquetted material. For thin-walled scrap in large dimensions stamping presses up to 400 MN are used to achieve bales of 1-2 t/m^3. The bales vary from 400×400×400 mm to 800×1000×1200 mm. Chips and turnings are also compacted in stamping presses, customarily in the form of small cylinders of 200 mm diameter and 150 mm height. With a density of > 2 t/m^3 such cylinders have a mass of about 10 kg. A density of > 2.46 t/m^3 would be desirable, because such briquettes charged into hearth furnaces would sink in molten aluminium and they would melt quickly and safely. Such a density can only be achieved by extrusion, which is a far too costly compacting process. For fine turnings roll compacting is most commonly used. Crushed and dried fine turnings are fed to rolling presses, which produce long, uncut bars. These are then cut into briquettes of optimal length with a density of near 2.3 t/m^3.

Example 12.3

A foil is baled to a cube of the format 0.4 × 0.4 × 0.4 m. The bale has a density of 2 t/m^3. The surface of this cube is 0.96 m^2. the specific surface is 7.5 m^2/t. The weight of this cube is 128 kg. The original foil in that cube had a surface of 56 million m^2. The *compacting of this foil reduced the surface by a factor of approximately 60 million to 1!*

12.2.6 Thermal treatment

Scrap contaminated by organic material, like swarf with cutting fluids, or packaging foils with PE, is usually thermally processed in order to remove material that is rather detrimental to the subsequent melting process. Scrap consisting of components with different behaviour at distinct temperatures is also thermally treated, like used beverage cans (UBC) (to separate lid and body alloys), aluminium scrap with heavy iron/steel inserts or hot dross. Organic material would generate a large amount of emissions when charged into a hot melting furnace. Furthermore carbon is a final product of the plastic cracking processes occurring inside a melting furnace when such particles are covered by salt. Fine carbon particles increase the viscosity of the salt flux drastically, which would result in difficult flux tapping or very high flux requirement. The removal of organic contaminations from aluminium scrap is therefore very important. Cutting fluid containing swarf is treated in rotary drums under reduced oxygen partial pressure, where water and organic matter are smouldered off. The off-gas is then burned at about 800°C. After magnetic separation the dried turnings or chips are stored under roof and melted under salt or compacted as described above. Combined paper-aluminium-PE foils used for soft drink containers are processed in order to regain the cellulose rather than the aluminium. The latter is collected in form of very fine tinsel after a gasification step. This aluminium still contains some residual carbon, which makes the re-melting of these fines, even after compacting, very difficult. This is also due to the effect of fine carbon particles on molten salt as described above. The reduction of the carbon content to below 1% and subsequent briquetting of this aluminium eventually results in a metal yield of about 65 to 70%. The flux requirement is still rather high and the total tonnage of aluminium, even from a large cellulose recycling plant is small. The economic viability of recovering aluminium in this way is dependent on the cost of producing the spangled aluminium. If the total costs of the process are borne by the recovered cellulose then the recovery of spangle-aluminium could be profitable. In 2001 in Europe (EU plus Norway, Switzerland, Turkey and Central and Eastern Europe) roughly 38 billion empty beverage cans were produced. The total world consumption is about 200 billion cans, of which approx. 85% are aluminium cans. The mass of beverage cans is continuously reduced by the decrease of sheet thickness, currently < 0.25 mm. At present, the average beverage can consists of the materials displayed in Table 12.8.

Table 12.8: Composition of the average beverage can in g/Used beverage can (UBC) or mg/UBC

Total mass	15.26 g
Mass of coating	390 mg
Mass of pigments	10 mg
Mass of oxide	125 mg
Mass of aluminium	14.65 g

Cadre 12.4

In the USA, the biggest consumer of aluminium beverage cans, part of the UBC is treated at about 580°C in rotary drums. The resin of the coating and paint and any organic left-overs inside the UBC are smouldered, the lid alloy AlMg5 is red short at this temperature *and fractioned. Simple screening allows the separation into lid and body alloy AlMg [359]. Alcan developed their Decoater process also based on a thermal step: Baled UBC (because of lower transportation cost) are shredded and treated by magnetic and eddy-current separation. On a heated vibration belt at 520°C the organic substances are thermally decomposed and the ashes screened off. In Europe the separation into lid and body alloy is not practised. However, combinations of rotary driers and hearth furnaces or multi-chamber hearth furnaces are used to smoulder off the organic content of UBC prior to melting in the melting furnace compartment. The smoulder off gas is used as fuel for melting. In Germany, where 85% of all beverage cans are still produced from tinned steel, sizeable amounts of aluminium made UBC are melted under flux (slat slag) in conventional rotary furnaces. Unprocessed UBC, however, force rotary furnaces to work simultaneously as smelters and incinerators, a task they were never designed for. At a temperature range of 520 to 590°C most of the cast aluminium alloys start to embrittle while the wrought alloys remain ductile. This principle could, rather simply, be used to separate cast alloys from wrought alloys. The fundamental concern of all thermal scrap treatment is the off-gas emission. To meet European standards crude off-gas is treated in after-burners at 800°C or higher. In order to meet the existing PCDD/F limit values, the off-gas must either be quenched to 80°C or have special absorbing additives added to it. The solid residues generated by the described thermal processes, like carbon or ashes or bag house dust, deserve particular attention regarding re-use or disposal.*

Example 12.4

A massive piece of scrap is covered by 0.16mm of oxides; its dimensions are 25 × 10 × 2 cm. A small individual particle of turnings, covered by an identical thick layer of oxides (density 2.9 t/m³) has dimensions of 15 × 2 × 0.5 mm. What is the wt. % content of oxides?

$Volume\ scrap = 250 \times 100 \times 20 = 500000\ mm^3$

$Volume\ metal\ core = (250 - 0.16) \times (100 - 0.16) \times (20 - 0.16) = 494890\ mm^3$

$Volume\ oxides = 500000 - 494890 = 5110\ mm^3$

$Mass\ metal = 494890 \times 2.7 = 1336.2\ g$

$Mass\ oxides = 5110 \times 2.9 = 14.8\ g$

$Content\ of\ oxides = 14.8/(14.8 + 1336.2) \times 100 = 1.1\ wt.\%$.

The same calculation delivers for the turning a content of 39.8 wt.% oxides, which are lost from the aluminium cycle! Eventually all NMC, wherever generated, end up at refiners, which also receive all the dross unavoidably generated on the surface of any unprotected molten aluminium and aluminium alloy. The salt flux as packaging material is the prominent NMC-outlet for any aluminium as oxide or other compound from the utilization cycle, which will be discussed in Chapter 13.

Chapter 13

Aluminium metal production

If 100% of the initial input could by returned to the aluminium utilization cycle and the growth rate of consumption (= production) would be zero, i.e. the primary metal demand would be zero t aluminium/a. Such an idealistic view allows the statement that primary aluminium production per year is the input necessary to compensate cycle (=system) losses and growth between January 1st to December 31st. Typical system losses of aluminium are:

- in chemical compounds, for example $Al_2(SO_4)_3 \cdot 18H_2O$ and $Al(CH_3COO)_3$,
- as an reaction agent for chemical processes, e.g. as reducing agent for aluminothermic processes, as sacrificial anode, as deoxidation agent for steel,
- metal not collected after its end-of-life, discarded or otherwise dissipated, and
- metal converted into non-metallic compounds during melting, fabrication, processing, use or recycling.

Presently Europe needs ca. 10 million t/a (± 1.5 million t depending upon the number of countries included within Europe). If the total amount of system losses would be in the order of magnitude of 60% of the input, the demand of primary aluminium metal would be 6 million t/a. To compensate, an average European growth rate of consumption of 3.5%/a, another 0.35 million t/a are required to close the European aluminium balance. The resulting 6.35 million t of primary metal demand/a is certainly in the correct order of magnitude and is provided to a substantial and increasing part by imports. Furthermore, often refiners need primary aluminium as feed material to dilute built-up troubling elements, for which no economically and efficient refining method exist yet. Primary metal has the highest dilution effect, but is most expensive, therefore refiners use as much low alloyed wrought scrap or primary dross as diluting metal as possible, with the consequence that primary aluminium demand will sharply rises with an increasing base-content of the element to be diluted. As long as large tonnages of primary metal are fed into the European aluminium utilization cycle the additional demand of primary metal as diluting metal remains latent. A fundamental principle of the aluminium utilization cycle is the accumulation of **N**on-**M**etallic **C**ompounds (NMC), regardless to time, location or method of its formation. Any piece of aluminium will be covered by a layer of oxides (between a few and several 100 μm thick), either naturally or artificially formed. The melting of aluminium scrap, covered by oxide layers (the smaller the piece or particle, the higher the relative content of oxides) is preponderantly a solid-liquid-separation rather than a pre-casting step.

13.1 Primary production of aluminium

This section will briefly discuss aluminium via electrolysis of alumina, which is produced from bauxite. A rule of thumb states that: 4 t of bauxite produces 2 t of alumina and 1 t of aluminium metal. According to a model of the European Aluminium Association (EAA)[365] the mass flows used are 4.111 t bauxite, 1.923 t alumina and 1.001 t liquid primary metal, while on a global average, the world production and consumption figures for 1991 and 1995 the ratios are [366]:

- 3.4 to 2.9 t bauxite/t alumina
- 2.3 to 2.2 t alumina/t aluminium metal

The differing data may be caused by unknown moisture content of the ca. 115 million t of crude bauxite mined in the years 1991 to 1995, the unknown average Al_2O_3 content of the bauxite and the unclear definition of what "aluminium production" in these data actually imply (e.g. liquid metal from cells or alloyed slabs and billets).

13.1.1 Alumina production

Alumina is a technical term for Al_2O_3 and its different modifications (α, γ and β), which is produced from Bauxite (see Chapter 11.1.1) via the Bayer process. Bauxites usually contain substantial amounts of minor constituents, including organic matter (e.g. Na-huminates), the Bayer process, however, is capable of producing alumina containing only harmless traces of minor constituents i.e. all the minor constituents such as Si, Ti, Ca, Cr, F, P, S are released with the iron containing residue red mud (the outlet of Fe, which is a major constituent of all bauxites), except Ga and V, both of which are separated from the leach liquor and produced as metal and salt respectively. There is a vast amount of literature available on detail on the Bayer process e.g. Ullmanns Encyclopedia of Technical Chemistry [367], which includes a long bibliography and information on the Bayer Process. The inevitable generation of red mud (red due to to large quantity of iron containing mineral) is one of the most precarious ecological burdens of aluminium winning. Krüger et al. [368] use an average number of 3.2 wmt red mud/t aluminium metal (*wmt=wet metric ton*). On the basis of these data about 75 million tons of moist red mud seem to be generated every year worldwide. Therefore much effort has been invested in the development of processes to convert red mud into a usable product. During the 2nd world war red mud was used in the iron and steel industry as a kind of iron ore. The application of red mud as colouring additive for the manufacturing of red roof tiles or coloured cement plaster could also be an alternative. Essential to this is the fixation of the high Na_2O content of red mud. Recently red mud was used for the production of flocculation aid for waste water treatment. An addition of sulphuric acid to red mud converted its Fe, Al and Ti content into water-soluble sulphates, which could facilitate the precipitation of dissolved inorganic salts or colloids. Nothing, however, is said about the residue from the sulphuric acid leach. At the moment there is little hope that these applications will, in the near future, significant contribute to the solution of the global red mud "problem", which occurs at the location of alumina plants (see Section 11.1.1). While 3.2 t of wet red mud are generated/t of primary aluminium metal from natural sources, about 0.5t of salt flux are eventually generated by melting casting aluminium alloys from industrial sources. For Europe these figures might be interpreted as follows (in contrast to red mud the salt flux is processed and its constituents completely returned to industry):

- 5.9 million t primary aluminium demand/a generate about 19 million t of wet red mud/a worldwide, and
- 2.1 million t of cast aluminium alloy production/a in Europe generate about 1.1 million t of salt flux/a, which is totally processed and its constituents recycled within Europe.

13.1.2 Smelting flux electrolysis

Claire-Deville constructed the first electrolysis cell for the winning of aluminium metal in 1854. The large-scale production of aluminium only became a viable proposition in 1866, when von Siemens developed the basics of heavy current engineering. Then in 1886 Hall and Harold simultaneously developed a process, which is still in use today. In 1888 Harold constructed the first aluminium primary smelting flux electrolysis in Neuhausen/Rhine-Switzerland, which resulted in the company known today as Alusuisse. One year later in 1889 in Pittsburgh/USA a second plant was constructed by Pittsburgh Reduction Co. the later Alcoa (Aluminium Company of America). To this day aluminium is produced by that process, just slightly modified and with regard to energy consumption drastically modernized. 100 years ago the electrolysis alone consumed 40 000 kWh/t of aluminium metal, now a consumption of 13 000 kWh/t aluminium is the state of the art. An electrolytic winning of aluminium from aqueous solutions is impossible, due to its high electrode potential and low hydrogen over voltage and reactivity with water. It is not the purpose of this chapter to add another work on primary winning of aluminium to the already existing numberless publications on this issue. Important features of the winning process steps are just mentioned to illustrate the differences to, and the reasons for, an entirely differing technology for secondary aluminium winning.

Smelting flux electrolysis is applicable, if the melting temperature of a metal compound is low or can be lowered by addition of salts. At first sight alumina (Al_2O_3) with a melting temperature of 2050°C seems to be unsuitable for this process. A mixture of molten cryolite and about 10.5 wt.% of pure alumina offer an eutectic temperature of about 962°C. By small additions of other salts, such as AlF_3, CaF_2 and LiF (also to adjust physical properties of the electrolyte, e.g. electrical conductivity) the melting temperature of the mixture is further decreased.

An electrolysis cell is a carbon-lined steel pot that works as the cathode. During operation the cell contains a bottom layer of molten aluminium metal (density ≈ 2.3 t/m^3) above which is a layer of molten electrolyte (density ≈ 2.1 t/m^3). The walls are usually lined with frozen electrolyte. From the top of the cell an anode made from baked carbon is submerged into the molten electrolyte. Many details in cell construction and several methods of continuous anode operation are applied, not changing the basic principles of the process. The net reaction of several complicated electro-chemical reactions is as follows (depending on cell operation also CO(g) can be created):

$$2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2 \tag{13.1}$$

An integral part any primary electrolysis plant is a cast house, for as mentioned earlier, aluminium is practically not used in unalloyed form. Here aluminium is converted into wrought alloy qualities and continuously cast into slabs or billets. Customarily 2-4 wt.% (of liquid aluminium) dross (containing primary metal or wrought alloy) is generated. Due to the large amount of electric energy required to produce aluminium metal (in 2002 the ca. 26 million t primary Al/a need power plants of a primary capacity of in the order of magnitude > 100 GW) primary electrolysis plants are built at places were electric power is cheap: Hydro-power plants in Norway, Canada and Russia, nuclear power-plants in France, USA. The European primary aluminium industry will in the long run most likely disappear due to its comparatively high cost for electrical power and the long transportation distances for bauxite or alumina. To minimize cost, the alumina plants are built near the bauxite mines or at least at the coast. Primary electrolysis plants are built near cheap electric power generators and simultaneously as close as possible to the next alumina provider; this favours all locations with hydro-power plants at navigable rivers (St. Lawrence river/Canada) or combinations of power plants and sea ports (Norway).

13.1.3 Other processes

The electrolytic winning of aluminium is complicated and expensive. For this reason industry has always tried to produce aluminium by direct reduction with carbon from its ore. Due to thermodynamics a temperature of >2000°C is necessary in order to accomplish this. At this temperature the liquid components (aluminium metal, oxide and carbide) do not show a miscibility gap, i.e. a one-stage reaction would just produce a liquid mixture of all 3 components. A 3-stage process has been developed and patented; numerous investigations followed, but as yet there is no feasible process. Different processes to win aluminium from aluminium chloride have been investigated. A 2-stage process has been developed and was operated on commercial scale in Germany until 1945, which was disassembled after 1945. Despite enormous improvements in the electrolysis technology and the resulting reduced production cost the "sub-chloride" process has never been commercially operated again. Recently the old idea of an $AlCl_3$-smelting flux electrolysis was realized in the USA in a pilot plant. It was reported that the energy consumption is less than that of the cryolite electrolysis, however, due to fundamental technical/engineering problems the operation was abandoned. Recently investigations have been intensified on the production of pure aluminium metal by refining of AlSi-alloys produced from aluminium-silicate ores. Other propositions such as the pyrometallurgical reduction of $AlCl_3$ by manganese (Toth-process) or the winning of aluminium metal via Al_2S_3 are still in the investigation phase [369].

13.2 Recycling of aluminium metal containing material

The production of one ton of aluminium from collected scrap requires only **12%** of the energy *(includes the processing of the resulting salt flux)* needed to produce the same ton of aluminium from bauxite. Material that does not contain aluminium in metallic form cannot be brought back to its former metallic properties by simple melting. Such material may become subject of special processes to convert it into compounds, which could be used in particular sectors, e.g. chemical or pharmaceutical industries. The conversion or refining of non-metallic compounds of aluminium into forms, which could be utilized anew, is considered recycling of non-metals. This section, however, is focused on the recycling of aluminium metal only. Refiners are those secondary aluminium smelters, which process all categories of scrap, including old, collected scrap and dross. Consequently all dross produced by "fluxless" smelters (the remelters) eventually ends up at refiners. The industrial "ore" scrap, contains prevailingly alloying elements of aluminium suc has Si, Cu, Zn, Fe, Mn, Mg, and impurities originating from typical aluminium applications in products such like Fe, Ni, Cr (in stainless steel), organic matter (e.g. plastic, oil, grease, paints, etc.). In contrast to the Bayer-Process for primary aluminium sources, no equivalently efficient refining technology is in use to separate those impurities from secondary aluminium sources (scrap). Therefore appropriate blending of scrap categories is one of the keys to melting collected aluminium scrap. Products manufactured out of aluminium alloys have fundamentally only two possible routes they can follow:

- They disappear from the utilization cycle as loss (lost aluminium metal):

  Metallic products end up in scrap of other metals and are eventually slagged during the winning of that respective metal (e.g. not separated aluminium in steel scrap).
  - Metallic products are not collected and disappear.
  - Metallic products that are or could not be separated end up in landfill or in incineration ashes (aluminium metal recovered from incineration bottom ashes is fed into the metal cycle again).
  - Metallic products are converted into chemical compounds that are irretrievably excluded from aluminium recycling (e.g. aluminium for steel deoxidation), even during melting when aluminium is converted into oxide and forms dross.

- They are fed into the aluminium metal re-cycle (recycled aluminium metal):

  Products manufactured from aluminium metal that have not disappeared or have been irretrievably converted into non-reducible compounds are available at the end of their lifetime as remeltable scrap. If the scrap is clean and little alloyed or of one alloy sort (usually new scrap), it is converted into ingots, slabs or billets at remelters. But with each cycle part of this little alloyed scrap is fed into the old scrap cycle were it is required as a dilution material for accumulated troubling elements.
  - The increased degree of contamination by coatings or foreign metal inserts (e.g. old scrap, collected scrap and dross) inevitably end up at refiners where they is melted under salt. The use of salt, however, unavoidably generates salt flux. This flux contains the valuable melting salt, sizeable amounts of entrapped aluminium alloy and NMC as the mineral end of all aluminium recycling. In this substance all products of oxidation and weathering or pigments from paints or coatings end up. Here we find the TiO_2 of printed UBC, the tiny glass reflectors of car number plates or traffic signs, the fine products of anodic oxidation, or simply the coarse oxide particles from metal burn in dross. The intermediate product that collects all these NMC companions of aluminium products is a salt flux. Although the word salt flux is a technical term, it is misleading since NMC particles are in a solid state even above 800°C, while the salt flux starts to melt above 650°C i.e. at the operating temperature of scrap melting. Therefore solid NMC particles and molten salt form a suspension, hence the salt flux it should rather be called high temperature slurry (HTS).

It is clear that the salt flux is of crucial importance to aluminium recycling, therefore substantial detail will be devoted to discussing its properties in the next sections. The following aspects that affect aluminium recycling will be discussed, (i) furnace charge, (ii) the furnace type with respect to the various fundamental aspects of the flux, and (iii) properties of flux such as viscosity, surface tension and density. It also provides a summary of work carried out in co-operation with the authors and the secondary aluminium smelter K. Konzelmann Metallwerke (KKM) in Germany to optimize metal recovery. The author's work work focussed on the following questions to achieve this goal:

- Is the amount of entrapped metal in salt flux a function of its viscosity?
- If so what parameters influence the flux viscosity?
- What reactor technology is best suited to recover the metal?

13.2.1 Re- or Downcycling?

It is tempting to use the percentage of primary material addition to any kind of second generation material in order to maintain its level of re-cycling to define the down-cycling. One should be careful with this definition since one must consider the complete material cycle to answer this well. Collected aluminium scrap is usually contaminated by numerous foreign metals, among those are iron, nickel, chromium. These elements are detrimental to quality standards but extremely costly to separate, if at all thermodynamically possible. The ultimate solution is to add primary aluminium metal to the melt in order to achieve the requested quality. The final alloy shall have <0.5% Fe. *Copper or tin in steel are another example for impurities for which no practical refining step exists. Well-aimed scrap preparation or dilution by pure steel is then the only alternative. Copper for use in electrical installations must have a high purity clearly defined by standardized chemical analysis, e.g.* < 15 *ppm S,* < 2 *ppm Se,* <2 *ppm Sn,* < 2 *ppm Bi, etc. Modern copper smelters and refineries are able to achieve these quality standards even when processing heavily contaminated scrap i.e. recycled copper can be returned to the industrial cycle of its primary use.* Therefore, the use of the fraction of pure primary material necessary to maintain the level of industrial application for recycled material is necessary but should be minimized not to downcycle the primary aluminium.

13.2.2 Preparation of charges

Secondary aluminium smelters or refiners produce standardized alloys that are ordered by customers. As feed material they use various scrap lots purchased days, weeks or even months before an order, since scrap is not always available on the market. Consequently scrap has to be stockpiled first. Both the melting of and delivery of scrap are batch processes. By trucks or train or ship, scrap lots of very differing tonnage are off-loaded at a smelter's scrap yard. Careful yard organization regarding lot weight, average metal yield and chemical composition as well as location at the yard is indispensable. Between 3 and 8 weeks of a smelter's scrap throughput is usually stockpiled at the yard. Layout and operation of scrap yards are subject to local and European environmental rules and regulations. Fluids stemming from scrap or rainwater effluents have to be collected and separately treated. In particular cutting fluids dripping from turnings or chips have to be collected in oil separators. The fluids have to be returned to the producers or otherwise re-used or disposed by the smelter. Lumpy scrap can be stored in open air, while bright and/or sheet aluminium scrap should be placed under roof, as water would immediately corrode the surface resulting in a loss of recovery. In particular in typical Continental European winters, scrap stored in open air is covered by ice and snow. This aggravates transportation (weight increase) as well as subsequent scrap processing, and severe explosions can occur during charging into hot melting furnaces. Water, snow or ice on scrap reduce the net weight of the feed, complicate the charge make up calculation and moreover absorb energy for water evaporation. It is desirable to store scrap under roof, which would keep it dry and reduce rainwater effluent problems. The area necessary for a scrap yard is a function of the bulk densities of scrap. Table 13.1 summarizes bulk densities of typical scrap material [360].

Example 13.1
A smelter with a throughput of 60 000 t scrap/a needs to store 11 000 t of scrap. The required area is roughly 10 000 m^2*. A roof spreading over this area cost about 200 €/*m^2 *or 2 million € capital investment, which has to be compared with the cost savings by easier and safer material handling and by lower melting cost (less wa-*

Table 13.1: Bulk densities of typical scrap material [360]

	Bulk-density (t/m^3)
Compacted offset material	1.34
Loose offset material	0.33
Compacted punching residues	1.66
Compacted burr of castings	0.77
Loose turnings	1-1.20
Chips	0.33-0.50
Bleedings	0.42
Beer barrels	0.11
Sheets	0.87-0.93
Wire	0.42
Rims	0.30
Bottle caps	0.11-0.13
Loose foils	0.16
Granulate	1.00
Castings	0.20
Dross	0.50
Profiles	0.14-0.17
Shredded scrap	0.56

ter in the scrap = more metal in the feed = less cost per t of produced metal).

Small scrap, like turnings, can only be stored under roof. If stored in open air rain would rapidly wash away the corrosion-prohibitive cutting fluids. Due to the high specific surface (>10 000 m^2/t) corrosion, and hence metal loss, would then increase drastically. Corrosion of turnings generates enormous amounts of heat, which could lead to self-ignition (because of the development of H_2). Besides metal and oxide, dross contains aluminium compounds like carbides, nitrides, phosphides and sulphides. These compounds are extremely reactive in contact with water, even with the moisture of the air. The said compounds spontaneously produce gases on contact with water. These gases are partly inflammable, partly toxic, like CH_4, NH_3, PH_3, and H_2S. Accordingly the storage of dross under roof is absolutely necessary. Alloying elements are essential parts of the feed of secondary aluminium smelters. Customarily these elements are delivered in small particle sizes to promote fast dissolution in liquid metal. To protect them against corrosion it is good practice to store them inside the smelter building in small mobile containers or boxes. Silicon, which is used in larger quantities, is usually stored in boxes outside the building, but under roof. Some smelters possess their own cutting equipment (e.g. guillotine shears) for material too large in size to pass the charging door of the melting furnaces. Others run their own magnetic separation station (in particular as an integral part of swarf processing and drying), partly supplemented by eddy-current separation.

Sampling

Upon off-loading of a new scrap lot a sample is taken. This sample has to be representative, i.e. it must represent the whole lot, and therefore it should have a minimum quantity. On the other side economic considerations and time requirements demand that this quantity be as small as possible. In practice a typical sample is between 20 and 100 kg. However, the necessary quantity is a function of the homogeneity of the delivered scrap lot. At least 5 different descriptions of the nature of scrap are used to stipulate the resulting sampling:

- homogeneous bulk material of uniform size (e.g. turnings),
- bulk material of very differing size-distribution (e.g. dross),
- lumpy scrap of one alloy only (e.g. offset sheets),
- lumpy scrap of several alloys (e.g. collected old scrap), and
- compacted scrap, not detachable (e.g. briquetted chips).

For each of these categories the smelters have their own rules for proper sampling which provides the following essential parameters:

- content of free iron, magnetic, and (if possible) iron in stainless steel,
- moisture content and loss of ignition (difficult),
- radioactivity; usually determined directly on the transport truck (it would immediately exclude the lot from acceptance),
- metal yield, and
- metal composition.

Metal yield and recovery

Only the metallic content of aluminium-alloys can be recycled by melting. It is extremely time-consuming and expensive to determine the metallic fraction of the aluminium content and all alloying elements of a scrap sample. Classical chemical analytical methods analyse the total content of aluminium, irrespective to how much of it is metal or bound to oxide or other compounds. The smelters need the metal content of all metallic elements only. The discrepancy between needs and reality has been bridged by a sample melting method agreed upon by metal traders and smelters alike. A scrap sample is melted under such a surplus of flux (customary kg flux: kg scrap = 1:1) that oxidation of the metal is practically excluded; in addition the flux is so fluid that almost no metal remains entrapped. The achieved metal yield of a sample melted this way is considered the maximum extractable metal content, traditionally equated with the metal content. The classical term of "recovery" is only meaningful if the metal content of a feed is known . By definition recovery relates amount of tapped metal to the original metal content in the feed. Secondary aluminium smelters, however, do not know the metal content in their feed material. Therefore the definition of recovery for a secondary copper smelter and that for a secondary aluminium smelter are different! Table 13.2 displays terms and definitions used for secondary aluminium smelters (the same would apply to secondary magnesium smelters) and could help to avoid misunderstandings.

Example 13.2

1 t of magnesium scrap resulting as residue from casting has to be melted in an induction furnace. The scrap particles are all over covered by a 50 μm thick layer of oxide. The measures of the average scrap particles are as follows, including oxide layers: 200 mm long, 10 mm wide and 1 mm thick.

Table 13.2: Terms and definitions used for secondary aluminium smelters

Unit	Sampling station	Melting plant	Incl. alloying and casting station
kg metal/ ton scrap input	metal yield	melting yield	plant yield
kg metal/ton metal content in scrap input	metal recovery	melting recovery	plant recovery

The scrap is melted in crucibles by addition of 10 wt.% of flux. The density of oxide is 3 and of the metal 1.7 t/m^3. 6% of the metal content of the scrap is oxidised during melting and converted into oxide. All oxide and the flux form dross, which when skimmed contain 25% of entrapped metal. What are the melting yield and the melting recovery?

Analysis of sample

The sample is melted together with flux in a small crucible or in a small rotary furnace. The metal is tapped and carefully weighed. The salt flux is controlled with regard to potentially larger pieces of entrapped metal, which would be separated, weighed and added to the tapped metal. If 50 kg of scrap were melted and the total amount of metal tapped is 46.5 kg, then the metal yield is 46.5/50 × 100 = 93%. A sample of the tapped metal is then analysed in order to attain its chemical composition. Under a charge number code the characteristic parameters of the scrap lot are computerized: Number of store box, total gross tonnage, moisture content, metal yield, and chemical composition. From these data the computer composes the scrap menu for each individual charge according to tonnage and the quality of the alloy ordered by the customer. The samples melting station of a secondary aluminium smelter corresponds to the classical analytical laboratory of a copper, lead or zinc smelter. Unfortunately the result of the sampling station is only a fair approximation to the metal content, but not the actual metal content that would be needed for a mass balance of the smelter or even of one individual furnace. For this reason one of the bigger secondary aluminium smelters in Germany's sampling furnaces (small gas-fired rotary furnaces) were calibrated (in cooperation with the authors) by using self-made standards. The result is unmistakable: The metal yield produced by these sampling furnaces under conditions of routine operation represent between 98.5 and 99% of the real metal content. These data is specific for this sampling station only, and must be tested for each sampling station individually. The 98.5% corresponds to the metal recovery of the sampling furnaces, the following example elucidating the importance of this value.

Example 13.3

80 kg of a scrap sample are melted in the sampling furnace.
The weight of the tapped metal is 72.6 kg.
The metal yield is 72.6/80 × 100 = 90.75%.
The metal content of the scrap sample is now 90.75/98.5 × 100=92.1%.

The known metal content of each charge is used to establish computer models for the mass balances of the large scale melting furnaces. The results of the mass balance using actual operation figures are compared with daily production data and validate the calibration. The results of the calibrated sampling furnaces and the mass balance model are the essential prerequisites to balance the complete smelter mass and energy balance (see Chapter 14).

Losses on plant due to oxidation

Before any aluminium alloy is rolled or extruded or cast it is liquid for a certain period of time. Liquid aluminium, however, exposed to oxygen containing gas (air, H_2O, etc.) inevitable generates oxide on its surface that is skimmed off, and thenceforward called dross. Products manufactured of aluminium alloys are partly artificially oxidized (e.g. for decorative purpose), or painted with inorganic pigment containing substances. During their lifetime aluminium products not protected by such coatings are exposed to air and moisture, which attack the surface. Whenever a new surface is created, e.g. by cutting, crushing, machining or milling, this surface is oxidized again. All these non-volatile **NMC** (non-metallic compounds) would accumulate by recycling, if not ejected somewhere in this utilization cycle. The oxidation rate of aluminium as published by Roth [370] as the increment of mass by oxidation is shown in Table 13.3. *For 800° C the increment is 26.5 mg oxygen/cm*^{2}*/hour, i.e. 56.3 mg of* Al_2O_3 *have been generated. This number is equivalent to 0.000156 mg oxide/mm*^{2}*/second, as published by Alfaro [371]. Several mass balance calculation have been carried out using the figures between 775 and 800° C and compared with actual melting results from practice. However, such figures remain meaningless since the time span scrap particles are exposed to the oxidizing furnace atmosphere where not provided.*

Table 13.3: Oxidation rate of aluminium at different temperatures[370]

Temperature (°C)	Oxidation rate $\left(\frac{mg}{cm^2 \times h}\right)$
700	12
775	13.5
800	26.5

13.2.3 Melting furnaces for scrap

Depending upon the degree of contamination of aluminium scrap by NMC and organic material, melting is carried out in different furnace types with or without salt.

Flux-free vs. melting under flux?

During the last two decades there were sometimes heated discussions about the so-called fluxless melting of aluminium scrap, versus melting under salt. The fluxless smelters claim to be environmentally friendly and pointed the finger at the producers of the salt flux waste. It was a helpful debate for it provoked a system-analytical look on the entire metal utilization cycles. When melting aluminium scrap one of the essential objectives is the separation of solid oxides from liquid metal. Due to the small difference of density between NMC and liquid metal very fine oxide particles tend to float in the molten metal, increasing its viscosity and causing endless problems when casting. Clean lumpy scrap contains usually $< 1\%$ NMC and is therefore usually melted in box-type furnaces without salt. Finely dispersed oxide particles are transported to the bath surface by purge gas treatment (N_2 and Cl_2) of molten metal, which is primarily to reduce the content of dissolved hydrogen. The surface of liquid metal in contact with burner off-gas (CO_2 and H_2O) oxidizes rapidly until the generated thin oxide layer prohibits further oxidation. The cumulated oxides are skimmed from the surface as dross. Scrap with a metal yield of < 95%, contains >5% NMC. This amount of NMC is by far too much to be removed by dross skim and metal filtration. Freshly skimmed hot dross contains about 65 to 80% liquid metal, entrapped predominantly by capillarity forces. Melting scrap with 95% metal content correspond to a charge of 950 kg metal and 50 kg NMC. Adding another 1% of oxide to the NMC by oxidation of molten metal, the bath composition would be: 950-10/1.9 − 945 kg metal, and 50 + 0.01 × 1000 − 60 kg NMC. If dross is skimmed with 65% metal, the mass of dross is 60/(1-0.65) − 171 kg. The tapped metal would then be 945-171 × 0.65 = 834 kg. The melting yield would be 834/1000 × 100 = 83.4%. Compared with the metal yield of the same scrap melted in the sampling furnace of 95 × 0.985 = 93.6% approximately 10% less melting yield would be absolutely unacceptable. A similar calculation for actual old, collected scrap, which contains rather 15% than 5% NMC, would produce an almost disastrous result. Therefore scrap with < 95% metal yield are generally melted in rotary furnaces under flux. The traditional channel for the NMC-outlet is the salt flux, generated by the refiners. At the refiners all dross, whether pre-processed or not, is melted under salt flux. The use of molten salt flux in a rotary furnace has two main functions to fulfil:

- it protects the scrap and liquid metal from oxidation, and
- it packages the NMC by adsorbing it, hence the vehicle of its outlet.

In fluxless operated furnaces the generated oxide layer on the molten metal works as the protecting agent, but there is no particular packaging material for the NMC. The only possibility is to skim the oxide skin at the end of a melting cycle (batch melting operation) or from time to time (in continuous melting operation). Due to the lack of a particular packaging agent the removal of dross is associated with a very high metal content: Hot dross contains 60 to 80% metal, it is therefore obvious that the development of dross has to be kept to a minimum, otherwise metal loss is higher than the original NMC content, about 1.5 to 2.3 t metal/t removed NMC, which is an intolerable value. When melting corroded aluminium scrap with salt, the molten salt layer is a highly suitable packaging agent for NMC[1]. The average metal content of salt flux is between 6 and 12% and the NMC content about 35 to 45%, referred to the mass of flux in the moment of flux tapping. In this melting system the metal loss is 0.15 to 0.25 t metal/t removed NMC. This is 1/10 of the specific metal loss of flux-free melting, or in other words, salt is a highly efficient NMC-remover with respect to associated metal loss.

Rotary furnaces for aluminium melting

Rotary furnaces fired with natural gas and air run about 4.5 up to 8 hours/cycle, those fired with gas and pure oxygen may run between 3 and 5.5 hours/cycle. The duration of a complete rotary furnace cycle (from metal tap to metal tap) is a function of:

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[1] As long as the charge is in solid or pasty state it is continuously lifted up by the rotating furnace wall until it tumbles back. This movement causes a desirable wrapping up effect, with each scrap particle being covered by a thin layer of molten salt shielding it from oxidation. In order to achieve this effect, salt is first charged into the furnace and melted; only then the scrap is charged. Since the charged scrap is cold the molten salt immediately freeze on the surface of each particle and it that way protects it until it starts to melt. Rotary furnaces are batch processes, i.e. for each furnace cycle different alloys can be produced.

- heat transfer (fuel-air or O_2 burner; flame temperature),
- retention time of hot burner gas (single or double pass),
- number of individual charges (layout of charging machine),
- bulk density of scrap (low bulk density needs more charges and time),
- efficiency of salt flux tapping (flux is tapped into flux ladle trains or singly provided ladles),
- skillfulness of furnace operators, and
- holding capacity of the furnace (5 to 60 t/charge).

Modern rotary furnaces have a holding capacity of 15 to 25 t/cycle (salt plus scrap together). It is obvious that more salt means less scrap; less scrap means less metal tapped. Consequently the almost fixed cost per cycle are divided by less metal, which result in higher melting cost in €/t metal. There are other good reasons to reduce the salt fraction of a charge, for more salt consumption corresponds with higher salt costs. A higher salt addition generates more salt flux, which results in higher salt flux disposal or treatment costs. Moreover the content of entrapped metal seems to be a rather constant value for a given smelter practice. Accordingly more salt flux corresponds with higher metal loss in flux. Higher fractions of salt in a charge cause dramatically increased melting costs. The holding capacity of a rotary furnace is the volume of the drum below the front/charge-end opening. For a rotary furnace with a 2.75 m inside diameter, an inside length of 5 m and a front opening of 0.9 m diameter the maximal usable volume is 8.7 m^3. This volume is filled by:

- 6.7 m^3 liquid metal and 2 m^3 liquid salt flux, which implies a capacity in tons of $6.7 \times 2.46 + 2 \times 2.0 = 20.5$ tons, or
- 5.5 m^3 liquid metal and 3.2 m^3 liquid salt flux, which results in a capacity is = 19.9 t.

The volume of a rotary furnace can be calculated assuming that it is simply a horizontal cylinder of d_i (m) internal diameter and L_i (m). The openings of the charge and off-gas end have a diameter of d_c and d_g (m) respectively. The lower rim of the charge end opening limits the useable volume. The cross area of the bath (salt flux plus metal) is:

$$A = \left(\frac{d_i}{2}\right)^2 \frac{\alpha}{360}\pi - \frac{1}{2}s \cdot \left(\frac{d_i}{2} - h\right) \quad (m^2)$$

The bath volume is given by

$$V = A \cdot L_i \quad (m^3)$$

The bath width is given by:

$$S - 2 \cdot [h \cdot (d_i - H)] \cdot \epsilon^{(0.5)} \quad (m)$$

$$\sin\left(\frac{\alpha}{2}\right) = \left(\frac{S}{d_i}\right)$$

$$H = \frac{d_i - d_c}{2} \quad (m)$$

For the given furnace data and for the given symbols in Figure 13.1, the derived quantities are $H = 0.925$ m; $S = 2.6$ m; $A = 1.74$ m^2 and $V = 8.7$ m^3. From industrial practice it is

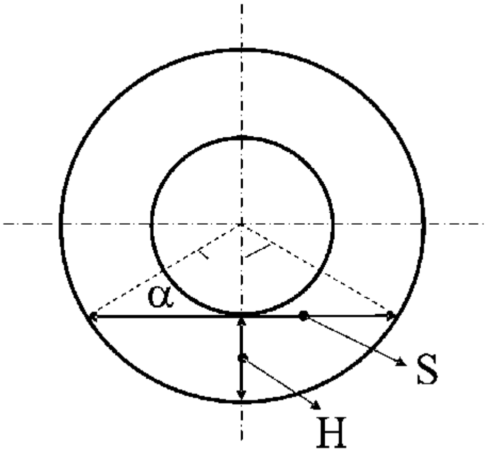

Figure 13.1: Cross section of a rotary furnace for aluminium recycling

known that about 70 kg of salt per furnace cycle is leaving the furnace by simple carry-over of salt-dust, evaporation and/or chemical reactions. This quantity is assumed to be independent of the amount of salt added per cycle, as evaporation is a function of time, temperature and evaporation surface. Time and temperature may statistically vary within a cycle whereas the evaporation area in a given furnace is a specific constant. For the given rotary furnace data the evaporation area is composed out of:

- the bath surface,
- the un-immersed covered shell, and
- the two un-immersed front sides of the drum.

The shell and the front areas are continuously diving into the wetting salt flux and are consequently covered by a layer of salt, therefore the total evaporation area is given by:

$$\begin{aligned}&2.6 \times 5 + \frac{360-\alpha}{360} 2.75\pi \cdot 5 + \pi(1.375^2 - (1.375 - 0.9)^2) \\ &+\pi(1.375^2 - (1.375 - 0.75)^2) = 13.0 + 26.15 + 5.23 + 4.71 \\ &= 49 \quad (m^2)\end{aligned}$$

For cycle times of 4 to 5 hours the specific evaporation rate is in maximum 290-360 g $\frac{\text{salt}}{\text{h} \cdot \text{m}^2}$. Table 13.4 gives a comparison between two cycles with different salt addition. The basis is a 20 t rotary furnace, the charge consists of salt and scrap with a metal yield (obtained from the sampling station) of 90%. The corresponding metal content of the scrap is 91.4%. The cost for salt and flux increase proportionally, but the most detrimental effect is the decreased melting yield from 85.6 to 84.9%, compared to the result of the sampling station of 90%.

The ongoing competition between the European secondary aluminium smelters has forced them to decrease cost. There are certainly many sectors in a smelter where cost could be

Table 13.4: Comparison between two cycles with different salt additions

Salt addition	13%		20%	
	t/cycle	kg/t metal	t/cycle	kg/t metal
Scrap	17.4	1165	16.0	1175
Salt	2.6	174	4.0	295
Total input	20.0		20.0	
Tapped salt flux	5.3	355	6.6	489
Tapped metal	14.9		13.6	
Cost for salt and flux (€/t metal)	41.50		60.20	

reduced, but hardly any measure results in such an immediate effect as minimizing salt addition to a rotary furnace. Minimizing provokes the question "what is the minimum?". To answer that question the afore mentioned rotary furnace is used, the salt addition is further reduced and the expected effects are discussed. The NMC-solids are dispersed in liquid salt and form a suspension or a slurry. Reducing the salt addition below 13 wt.% of the total charge (2.6/20.0) is equivalent to increasing the fraction of solids in the molten salt. At a certain volume percentage of solids the slurry all of a sudden turns into a more pasty constitution; a bit more NMC-particles - or little less salt - and the slurry is solid. Neither a pasty nor a solid salt flux can be tapped from a rotary furnace. Therefore the ratio salt:NMC should be safely kept above this sticking point. Over decades the furnace operators developed a kind of instinctive assessment of the tonnage of salt necessary to guarantee a smooth, unproblematic and therefore short furnace cycle. From this experience the so-called salt factor has been derived which is the ratio "ton of salt added:ton of NMC in scrap". A salt factor (SF) of 1.5 implies that 1.5 t of salt are charged into the rotary furnace per ton of expected NMC in the scrap. The basis of the NMC calculation is the metal yield (MY) resulting from the sample melting. Since the MY represent the fraction of a scrap sample that is pure metal while (100% MY) equals the % NMC in the scrap. The rotary furnace operators use a very functional relationship to determine the amount of salt to add:

$$M_{salt} = M_{scrap} \times \frac{100\% - \%MY}{100} \times SF \quad \text{(t/cycle)} \tag{13.2}$$

$$M_{salt} + M_{scrap} = \text{holding capacity of the rotary furnace (t/cycle)} \tag{13.3}$$

In the recent past salt factors of 1.6 to 2 were traditionally used producing a salt flux with a sufficiently low viscosity i.e. the flux consistency is always on the very safe side. After salt flux processing became mandatory the smelters were forced to reduce the salt addition, i.e. the salt factor (SF), to compensate the drastically increased salt flux disposal cost. At present salt factors of 0.9 and 1.5 are used, depending upon the type of scrap and its degree of contamination. These salt factors still do not represent the minimum salt:NMC ratio, they simply reflect the limits of practical experience. Cyclic scarcity of scrap, continuous reduction of emission limit values by the authorities, enormous market power concentrated at the metal buyers (automobile manufacturers), import of cheap alloys from abroad, etc. will maintain an ongoing pressure on the smelters cost. There is no other choice than to analyze in detail the salt flux properties in order to find out the optimal salt:NMC ratio for each individual scrap category, since the times for using simple empirical salt factors are over.

Example 13.4
A 15 t furnace is charged with scrap with an average metal yield of 87% and a salt factor of SF=1.25. The amount of salt to be added to the charge is therefore given by:

$$M_{salt} = M_{scrap} \times 0.13 \times 1.25 \tag{13.4}$$

$$M_{salt} + M_{scrap} = 15 \quad (t) \tag{13.5}$$

$$M_{scrap} = 12.9 \quad (t) \tag{13.6}$$

$$M_{salt} = 2.1 \quad (t) \tag{13.7}$$

Cadre 13.1
The traditional melting theory postulated that scrap with identical melting yield shall require the same amount of salt to guarantee a fluid salt flux. However, in contrast to this theory the melting practice knew always scrap types that required significantly higher amounts of salt to generate a fluid salt flux, e.g bottle caps with inlaid plastic seals, lacquered UBC and foils. Expressed in a salt factor, bottle caps should theoretically need a salt factor of 1.4, in reality any salt addition below 4-5 salt factor generates a pasty salt flux extremely difficult to tap from the rotary furnace. The large amount of salt added to these abnormal but valuable types of scrap (low alloyed wrought alloys) generate a huge tonnage of salt flux, which increases metal loss and operating cost as well. A further aspect plagued the refiners, the entrapped metal in salt flux that leaves the smelter as a loss! After flux processing this metal, which has already been purchased and melted by the refiner has to be re-purchased from the flux processor and melted again.

Melting processes using salt factors >1 and hence producing a liquid salt flux are called "wet melting processes". Salt factors of significantly lower than 0.8 produce a salt-NMC mixture that should rather be called a salt cake than a salt flux, with a pasty consistency making tapping impossible. Melting aluminium scrap with salt factors << 1 - customarily 0.5 - is called a "dry melting process" since no liquid salt flux is produced. To handle such salt cakes tiltable rotary furnaces have been developed resembling the rotating concrete transportation vessels or top blown rotary converters used in the steel industry. Tiltable rotary furnaces have only one furnace opening, fed through the open door, which holds the burner when closed. The off-gas outlet is also integrated into the furnace door. Most tiltable rotary furnaces are fired with gas and pure oxygen, which generates 70% less off-gas volume than gas-air burners. The flame temperature is about 2900°C whereby heat is transferred predominantly by radiation; with conventional gas-air burners the flame temperature is significantly lower and heat is prevailingly transferred by convection. Moreover the retention time of the hot off-gas is higher than in conventional rotary furnaces, due to the smaller volume and the doubled flow length, as gas inlet and outlet are on the same end. The higher the NMC content of a scrap the more pronounced the benefits of tiltable rotary furnaces are.

Example 13.5
Scrap with a metal yield of 95 and 85% respectively are melted in parallel in a conventional rotary furnace (CRF) with a salt factor of 1.3 and a tiltable rotary furnace (TRF) with a salt factor of 0.4. For comparison, the salt demand is shown in Table 13.5.

Table 13.5: Salt demand for Example 13.5

Metal yield:	95%	85%
Required kg salt/t scrap		
SF 1.3 (CRF)	65	195
SF 0.4 (TRF)	20	60
Salt savings	-45	-135

Despite the decreased holding capacity of tiltable rotary furnaces and the strict control required for their operation the advantages are convincing. Gas-oxygen burners and/or double-pass of off-gas improve the operation of a conventional rotary furnace; e.g. by placing the burner and the off-gas outlet on the opposite site of the charging door the hot flame and flue-gas have to pass the whole length of the furnace twice. This double-pass leads to an improved heat transfer and shortens the furnace cycle time. When calculating the scrap charge, the refiners disregards high and low metal yield and aims at a distinct alloy composition. The tiltable rotary furnace is particularly suitable for scrap with low metal yield, i.e. dross. Model calculations resulted in the proposal to melt dross and scrap in different furnaces: Scrap in conventional fixed axle and dross in tiltable rotary furnaces. The following data represent the model calculation that has been validated and has proven to be in the right order of magnitude.

Metal yield of dross	60%
Metal yield of scrap	90%

Joint melting

Salt required	247 kg/t feed
Salt flux produced	463 kg/t feed
Metal produced	775 kg/t feed
Salt – flux cost	55 €/t metal produced

Separate melting

Salt required	139 kg/t feed
Salt flux produced	360 kg/t feed
Metal produced	779 kg/t feed
Salt – flux cost	39 €/t metal produced

Three physical properties of scrap are found to be of crucial importance for the selection of the melting furnaces:

S/M	surface:mass ratio of average scrap particles (m^2/t),
LoI	loss of ignition i.e. the content of organic material (wt.%), and
NMC	content of non-metallic components. (wt.%)

By the application of Table 13.6 scrap can easily be characterized into its high-low assessment of the three important parameters, making it possible to select the most preferable melting furnace (summarized in Table 13.7). Clean small scrap with a specific surface of >1000 m^2/t ($m^2/t = mm^2/g$) can be melted without burn-off loss if submerged in liquid aluminium. This can be achieved effectively by pumping liquid metal (by mechanical or electro-magnetic pumps) into a kind of "toilet-bowl" forming a vortex into which the scrap fines are charged

Table 13.6: Scrap characterisation

		S/M		LoI	
		high	low	high	low
NMC	high	dross fines	dross lumps	sink-float scrap	dross; corroded castings
	low	turnings, chips	bleedings, clean sheet, billet residue	printed foils bottle caps	bleedings, clean sheet, billet residue
S/M	high	-	-	swarf, oily chips	granulate recovered from salt flux
	low	-	-	plastic coated or printed sheet, profiles with plastic inserts	sheet, massive castings

Table 13.7: Furnace selection

		Rotary furnaces		Non-rotating furnaces		
Salt:NMC ratio		> 1	< 1	0		
Furnace type		Fixed axle rotary furnaces	Tiltable rotary furnaces	Conventional hearth or box type furnaces, crucible furnaces	Hearth furnaces with SMM equipment	Multiple-chamber hearth furnaces
Content in scrap	NMC	high	very high	very low	low	low
	S/M	middle	low	very low	high	low
	LoI	low	middle	low	low	very high

und sucked in. ***This Submerged Melting is abbreviated as SMM in Table 13.7.*** For mechanical metal pumps ceramic rotors, which break easily, have to be used (steel or cast iron would be dissolved by liquid aluminium). Electro-magnetic pumps, however, are very sensitive to finely dispersed oxide particles in the metal due to their abrasive action. Such oxide particles tend to settle on the walls building up a electrically insulated layer, which reduces the pumping efficiency thereby promoting the settling even more. An elegant way of submerged melting of clean and homogeneously sized small scrap (e.g. de-lacquered and shredded UBC) is a vortex-type of mixer, by which liquid metal, liquid salt and solid scrap are intensively mixed - similar to a mixer-settler unit, frequently used in the chemical industry. In an adjacent settling chamber the formed salt flux can overflow and the molten metal return through an under-flow into a box-type melting furnace. Complete off-the-shelf SMM-units can be attached to any hearth furnace, partly including purge gas agitating device. For the melting of low NMC-containing scrap there are numerous variations of box-type furnaces, with side-well, open-well or subdivided into multiple compartments (closed-well Furnaces). These furnaces consist of 2 or more chambers. The first chamber is dedicated to burning off organic substances, the off-gas is then used as fuel in the melting compartment. Besides dross management (including usage of particular flux systems for improved metal coalescence) the minimization of energy requirements and emissions is of utmost importance for European secondary aluminium smelters. Very clean scrap of one alloy only can also be melted in low frequency induction furnaces. These furnaces need a closed current circuit in which melting can only be started with already liquid metal or at least massive pieces of scrap.

13.2.4 The properties of the salt flux for aluminium melting

An efficient flux shall protect the aluminium metal from oxidation and absorb as much NMC as possible. Preconditions for a good flux are:

- does not chemically react with aluminium metal,
- has a slightly lower melting temperature than aluminium alloys,
- has a lower density than molten metal,
- the salt does not decompose at temperatures around 800°C,
- no significantly evaporation at temperatures around 800°C,
- it has a low viscosity,
- it does not attack the refractory lining of the melting furnace, and
- the molten salt has a low surface tension.

Flux in contact with the chemically reactive liquid aluminium metal needs to be free of any oxygen containing compounds such as carbonates, sulphates, phosphates, borates and nitrates otherwise these react explosively with aluminium forming carbides, sulphides, phosphides or nitrides, combinations of alkali- and earth-alkali-chlorides meet this requirements and will be used as a synonym for melting salt or flux. Using the most appropriate melting salt (flux together with a coalescence supporting additive) is crucial for ensuring a high recovery of aluminium alloys from scrap with high NMC contents. Collected old scrap with different kinds of coatings, paints, inserts and dross represent this type of scrap.

The melting salt used in Europe is traditionally a blend of 65-75 wt.% NaCl, 25-30 wt.% KCl (average ratio NaCl:KCl = 70:30) and as surface active agent 2-5 wt.% CaF_2. Over decades Kali & Salz/Germany have provided the flux under the brand name Montanal. This NaCl:KCl ratio is representative of the KCl cut-off grade of underground salt mining in Central Europe, which focuses mainly on the winning of KCl. The binary system NaCl-KCl reveals an eutectic point at 50 mol% NaCl and KCl, with a melting temperature of 645°C, whilst the 70/30 flux has a liquidus-temperature of 725°C. Due to its lower melting temperature the eutectic blend is used in the USA. However, in Europe the price of KCl is remarkably higher than in USA, therefore European smelters still use the 70/30 blend.

Density of the salt flux

The density of the salt flux in liquid state at about 750°C is [360] 1.57 g/cm^3, and about 1.54 g/cm^3 at 800°C. However, numerous tests with salt fluxes from a secondary smelter resulted in quite different data by the authors. During these investigations volume and mass of freshly tapped salt flux were analysed and only the range of densities listed in Table 13.8 close the balance of measured mass and volumes.

Table 13.8: Densities measured by the authors

	Density (g/cm^3)
Solid NMC	2.9-3.1
Liquid flux	1.71-1.84
Liquid alloy	2.45-2.48

Surface tension of the salt flux

An important factor for the melting of scrap under flux is its surface tension, as it determines all physical phase transitions i.e. the kinetics of melting. It is desirable that metal droplets have a chance to coalesce, which requires the removal of oxide skins. A skin around a pure aluminium droplet consists of pure Al_2O_3 and has a surface tension of 865 mN/m at 800°C [360]. The surface tension of molten 70/30-salt is about 1/10, and can be further reduced by small additions of alkali-fluorides. The removal of oxide skins requires defects in these skins. Since the aluminium alloys are melted, the oxide skins do not consist of pure Al_2O_3 but of several oxides of alloying elements. The more aluminium is alloyed the more likely that intermetallic phases form oxides with significantly lower surface tensions, i.e. defects in the oxide skins increase with the concentration of alloying elements. Strong oxide skins (like pure Al_2O_3) need intensive mechanical shear force to rupture it or require an aggressive flux attacking the oxide skin by chemical reactions or drastic reduction of surface tension. Oxide skins with many defects (from alloyed aluminium) need a much less aggressive flux and may already be destroyed by mechanical forces provided by the rotation of the drum. Clean wrought and cast alloys of similar size show different melting behaviour. Clean wrought scrap needs more aggressive coalescence promoting additives, like cryolite, than cast alloy scrap that is efficiently meltable with CaF_2 as a coalescence additive. Aluminium alloys do not oxidise stoichiometrically, otherwise the NMC separated from the salt flux should correspond to a composition close to the most frequently used cast alloy AlSi9Cu3. Table 13.9 compares the oxide composition of NMC from salt flux at ALSA (Salt processing plant in Hannover, Germany) with those of a stoichiometrically oxidized alloy 226.

Table 13.9: Composition of NMC in practice and theory

	Oxides separated from salt flux wt. %	Oxides from alloy AlSi9Cu3 wt. %	Ratio ratio Col.1:col.2
Al_2O_3	58-70	82.87-87.95	0.8
SiO_2	7.0-12.8	9.09-12.53	0.9
CuO	≈0.5	1.33-2.33	0.4
ZnO	≈0.12	0.79-0.8	0.16
FeO	1.35-1.80	0.55	3
TiO_2	0.08-0.2	0.13	1
MnO	≈0.2	0.07-0.34	1
MgO	6.7-9.5	0.09-0.44	15

The relation between the two columns in Table 13.9 indicate that Mg and Fe oxidise over-stoichiometrically. Ti, Mn and Si stoichiometrically, Al, Cu and Zn under-stoichiometrically. The aluminium-oxide content of NMC from salt flux is distinctly lower than that of the alloy. In fact the aluminium content of the average of all melted scrap is expected to be even higher, for a large fraction of scrap is wrought alloy, i.e. much less alloyed. Aluminium alloys consist of numerous intermetallic phases (e.g. Al(n)Si(m) or Al(t)Cu(s) where n, m, t and s represent %) that oxidize on the surface but do not form a dense and protective oxide skin. Most of these mixed oxides adhere rather loosely to the metal and can be removed mechanically. Highly alloyed castings not coated by an electro-galvanized oxide layer look dull and pitted after a while, whereas little alloyed products maintain a long-lasting brightness. This is again proof of the difference between the properties of oxide skins on unalloyed and highly alloyed aluminium scrap: Mixed oxide layers are less dense as part of its oxide particles are just loosely fixed. During melting in a rotary furnace those oxides are easily washed away by molten salt. During the last 20 years several publications [365, 372, 373] focused on the coalescence effect of various fluorides (added to typical chloride-flux) on molten aluminium. The gist of the findings is summarized in the following list of additives, displayed in the ranking of increasing coalescence-efficiency.

$MgF_2 < CaF_2 < AlF_3 < NaF < LiF < KF < Na_3AlF_6$

Unfortunately the most ineffective are the cheapest chemicals and vice versa. However, as explained, only little or unalloyed clean scrap need salt with highly efficient coalescence additives. The oxide layer of typical cast alloy scrap is efficiently pealed off by rotation of the furnace and the 2% CaF_2 added to melting salt.

Viscosity models

The viscosity of molten 70/30-salt is about 1.45 mPa·s at 800°C [360], however, it is strongly dependent upon the content of added alumina particles. In research work by the authors [374] it was proven that the relationship between dynamic viscosity and wt.% concentration of Al_2O_3 does not reflect reality, as incorrectly stated by Krone [360]! It was found that it is predominantly a function of particle size distribution; either way the volumetric concentration of solids is important, i.e. weight % of solids are meaningless without their respective density. Viscosity is the resistance of a fluid to flow as defined by Newton (Eq. 13.8). This is derived

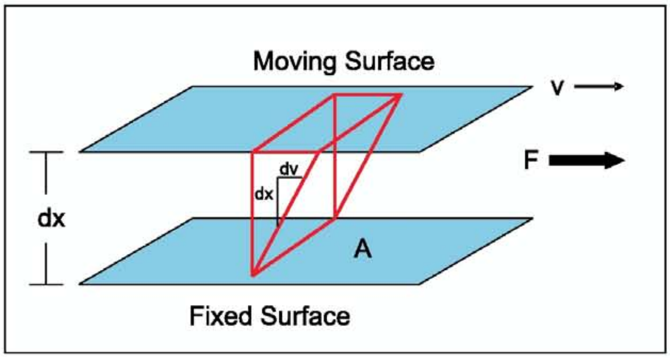

Figure 13.2: Viscosity model defined by Newton

by considering a fluid between two parallel plates of equal area A and separated by a distance dx as shown in Figure 13.2 and stating that a force F will maintain the difference of speed v of the two plates. Therefore, according to Newton all materials have a viscosity that is independent of the shear rate, implying that twice the force on a fluid would move it twice as fast. However, this is not valid for all systems, since not all systems have a constant relationship between shear stress and shear rate. These non-Newtonian fluids/suspensions are characterized by the suspending medium and the characteristics of the suspended solids, which include:

- the size and shape of the solids, and
- the solids concentration.

$$\text{shear stress} = \text{viscosity} \cdot \text{shear rate} \rightarrow \frac{F}{A} = \mu \frac{dv}{dx} \tag{13.8}$$

$$\mu = \frac{(F/A)}{(dv/dx)} \quad \left[\frac{N/m^2}{s^{-1}} = \frac{kg}{ms} = Pa \cdot s\right] \tag{13.9}$$

Newtonian fluids Suspensions that contain spherical shaped particles of 50 μm and have Newtonian characteristics; the viscosity of these suspensions is a function of the volume concentration of solids.

Non-Newtonian fluids Suspensions of smaller and/or asymmetrically shaped particles are non-Newtonian; the viscosity called an "apparent viscosity". There are several types of Non-Newtonian behaviour, characterised by the way the fluid's viscosity changes in response to variations in shear rate, the most common types being Bingham, Dilatant and Pseudoplastic. In Figure 13.3 the apparent viscosity versus shear rate for different types of time independent non-Newtonian fluids is shown, the dotted line depicting the viscosity versus shear rate for a Newtonian fluid.

Some non-Newtonian fluids even show a change in viscosity with time under conditions of constant shear rate, these fluids are time dependent and are called thixotropic or rheopectic. Table 13.10 gives some examples of the various different types of viscosities, however, some suspensions have a mix of properties i.e. therefore this classification is too simple.

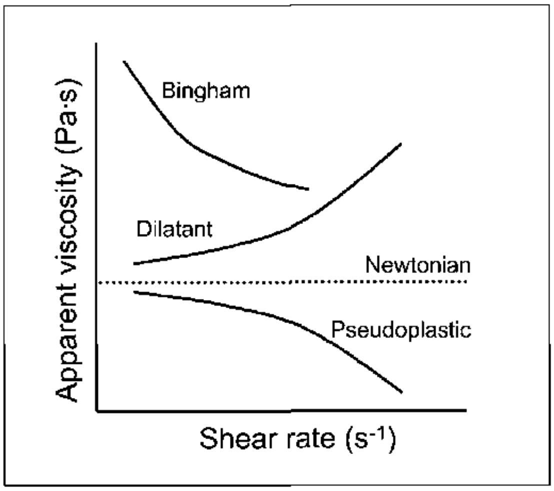

Figure 13.3: Apparent viscosity versus shear rate

Table 13.10: Viscosity types and materials [375, 376]

Type of viscosity			Example
Newtonian			sugar water most motor oils clay slurry
Non-Newtonian	Time in dependent	Bingham	tooth paste hand cream
		Dilatant	wet sand starch and water
		Pseudoplastic	shampoo ketchup
	Time dependent	Tixotropic	yoghurt most paints
		Rheopeptic	gypsum paste

Influence of volume-% solids on viscosity An important effect of the addition of solid particles to a fluid is their influence on the suspension viscosity. The viscosity will increase and often result in non-Newtonian behaviour. There are various derived relations between viscosity and volume percentage of solids, some of which will be discussed in this paragraph. These will subsequently be used to determine the constants in the relationships between viscosity and volume percentage of solids, hence modelling experimental data measured by the authors.

Newtonian liquids with a viscosity described by Einstein These suspensions of spherical particles have such a high dilution (below 10 volume-% solids) that interaction between the particles can be neglected [377].

$$\frac{\mu_m}{\mu_0} = 1 + 2.5 \cdot \Phi \qquad (13.10)$$

where

μ_m = viscosity of the suspension
μ_0 = viscosity of the suspending medium
Φ = volume percentage of solids

Suspension viscosity described by Thomas In more concentrated suspensions the various types of particle interactions influence the viscosity [377] as defined by Eq. 13.11.

$$\frac{\mu_m}{\mu_0} = 1 + K_1 \cdot \Phi + K_2 \cdot \Phi^2 + K_3 \cdot \Phi^3 \qquad (13.11)$$

where

K_1, K_2, K_3 = constants to be fitted to data

After the analysis of a large quantity of published data, Thomas derived Eq. 13.12 for suspensions with spherical solid particles.

$$\frac{\mu_m}{\mu_0} = 1 + 2.5 \cdot \Phi + 10.05 \cdot \Phi^2 + A \cdot e^{(B \cdot \Phi)} \qquad (13.12)$$

where

A, B = constants to be fitted to data

For all values of A and B in Eq. 13.12 the beginning of the curve is linear and starts to increase exponentially after reaching a critical volume percentage of solids (Figure 13.4).

Suspension viscosity described by Gay, Nelson, Armstrong The suspension viscosity described by Gay, Nelson and Armstrong [377] is defined by Eq. 13.13.

$$\frac{\mu_m}{\mu_0} = e^{\left[\left(2.5+\left(\frac{\Phi}{\Phi_{max}-\Phi}\right)^n\right)\cdot\frac{\Phi}{\Phi_{max}}\right]} \qquad (13.13)$$

where

n = constant to be determined from data
Φ_{max} = maximum volumetric concentration attainable (the motion of solid particles becomes inhibited because close packing is approached

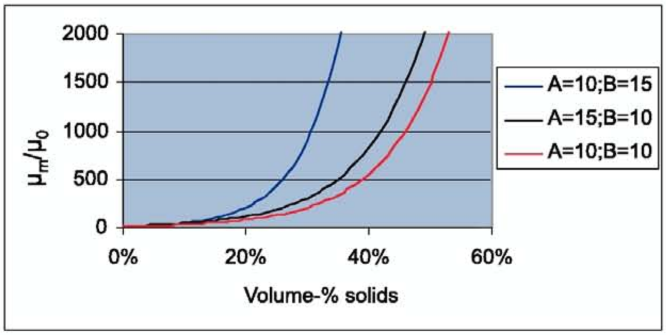

Figure 13.4: Viscosity versus volume percentage of solids (Eq. 13.4)

The value of Φ_{max} in Eq. 13.13 varies for different particle size distributions. Monodispersed suspensions have lower Φ_{max} values than heterodispersed ones, in which the smaller particles can settle between the holes of the large particles. So broadening the particle size distribution is expected to lead to a lower viscosity. For equisized spheres, a closed packed situation is reached for Φ=0.74.

Suspension viscosity described by Einstein-Roscoe The suspension viscosity described by Einstein-Roscoe [378] is given by Eq. 13.14.

$$\frac{\mu}{\mu_0} = (1 - \alpha \cdot \Phi)^{\beta} \tag{13.14}$$

where

α, β =constants to be fitted to data

The reciprocal value for (i.e. $1/\alpha$) in Eq. 13.14 represents the maximum amount of solids present in the flux before it starts to freeze. *(e.g. The viscosity of a CaO-MgO-Al_2O_3-SiO_2 melt containing spinel particles at 1646K is affected by the particle size. The measured viscosity of the melt was adequately modelled by an Einstein-Roscoe type equation [378]. The value of α for fine particles in Figure 13.5 is 4.24. The reciprocal value is 0.236. This means that the maximum amount of solids in the flux before it freezes is 23.6%.)*

Viscosity of suspensions with more than 15 Vol-% solids Two empirical equations for suspensions with more then 15 volume percent of solids are the Mooney (Eq. 13.15) and the Dougherty-Krieger (Eq. 13.16) equations [379].

$$\frac{\mu_m}{\mu_0} = e^{\left(\frac{2.5\Phi}{1-\Phi/\Phi_{max}}\right)} \tag{13.15}$$

$$\frac{\mu_m}{\mu_0} = \left(1 - \frac{\Phi}{\Phi_{max}}\right) \tag{13.16}$$

Parameters influencing flux viscosity in the following various parameters that affect flux viscosity will be discussed.

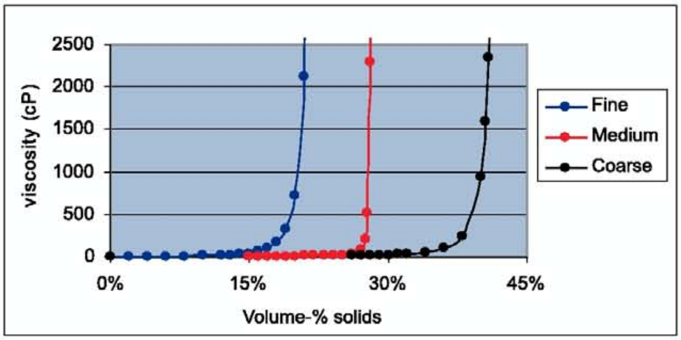

Figure 13.5: Viscosity versus volume-% solids (Eq.13.14)

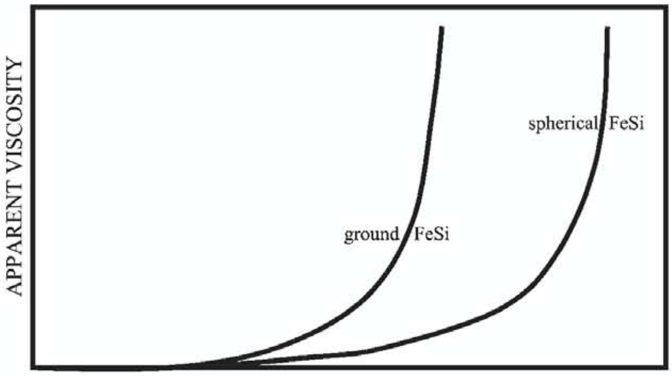

Figure 13.6: Influence of different shapes on the apparent viscosity

Temperature The viscosity of suspensions decreases with a higher temperature. This is a very important and difficult parameter in the flux layer. The temperature is not in the whole flux phase the same. E.g. the temperature in the flux where the paddles dive into the flux will be higher then where the paddles leave the flux.

Amount of solids in the suspending medium When the volume percentage of solids increases the suspension viscosity will also increase.

Particle size distribution of the solid NMC particles The coarser the solids the less viscous will the suspension be. For example, the salt flux of a furnace cycle where only used beverage cans are melted needs due to very high viscosity an enormous surplus of salt to stay liquid. The pigments on the beverage cans are extremely small and influence the flux viscosity already at small volume percentage.

Shape of the solid NMC particles Round particles produce less viscous suspension than angular ones (Figure 13.6).

Figure 13.7: Aluminium droplets collected from a salt flux after melting

Composition of the liquid salt Different elements (K, Ca, F, C) will have a different effect on the viscosity of the salt and therefore on the viscosity of the flux. The preferred evaporation of KCl with its lower viscosity then will certainly have an effect on the flux viscosity.

Feed material The properties of the NMC particles are depending upon the charge of the furnace cycle.

Estimation of salt flux properties

Industrial flux samples were taken at the KKM plant in Hannover and Neu-Ulm . These samples represent the reality and give the best view on what exactly happens in the flux phase formed during the process in the rotary furnace supplemented with experiments were done with a high temperature viscometer.

f-test, t-test and Weibull function The flux samples taken at KKM in Hannover and Neu-Ulm show a wide variety in aluminium content, aluminium droplets, NMC particle size, thickness and NMC/Salt ratio. To find out whether a relation between the different samples coming from different cycles exists, some statistic methods were used. It is important to keep in mind that all these samples come from different cycles with other feed material properties.

f-test The f-test is done to find out what the probability is that two cycles (from which 12 samples were taken at different positions in the furnace) have the same variance.

t-test The t-test determines whether two samples are likely to origin from the same two underlying populations with the same mean. This t-test is carried out on the different aluminium droplets that were present in the various samples of different cycles, Figure 13.7 depicting aluminium droplets of three different size classes.

Weibull distribution The Weibull distribution is applied on the 7 independent cycles to find out what the distribution of the different samples from one cycle concerning NMC/salt ratio is. The Weibull probability density function is given by Eq. 13.17 (also see Figure 7.3).

$$f(x) = \frac{\alpha}{\beta^{\alpha}} x^{\alpha-1} e^{-(x/\beta)^{\alpha}} \tag{13.17}$$

where

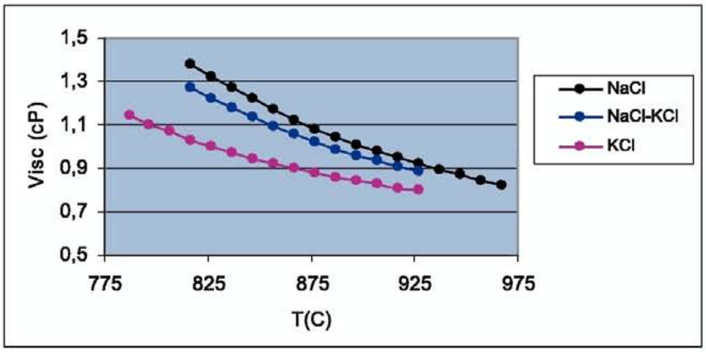

Figure 13.8: Viscosity of salt versus temperature for the three different salt mixtures

x = NMC/Salt ratio
α = shape (slope) parameter
β = scale parameter

Salt, aluminium and NMC properties

Salt density According to literature the density of salt at 750°C is 1.56 g/cm^3. But according to previous furnace models developed by the authors, the density of liquid salt must be higher. In these furnace models the mass balance could not be fit for a density of 1.56 g/cm^3. By melting salt in a crucible with known volume the mass and volume were measured and a density of 1.77 g/cm^3 was calculated. Table 13.11 shows the outcome of three independent experiments. The density of this salt may also be slightly higher because of the addition of CaF_2. The salt density in further calculations is the mean value of the theoretical and experimental density, therefore 1.67 g/cm^3.

Table 13.11: Salt density determined experimentally by authors

Experiment	Mass salt (g)	Volume salt (cm^3)	Density (g/cm^3)	Average (g/cm^3)
1	239	135	1.77	1.77
2	239	140	1.71	
3	240	130	1.84	

Salt viscosity The viscosity of salt is shown in Figure 13.8. These salt viscosities were measured with "the oscillating ball technique". The viscosity of pure molten salt flux is the similar to that for water at room temperature, however, it may significantly be increased by fine carbon particles originating from pyrolized paint coating (average 1 weight-% in salt flux) and fine NMC particles that are smaller than 10μm.

Aluminium density The density of aluminium is 2.47 g/cm^3 at 800°C.

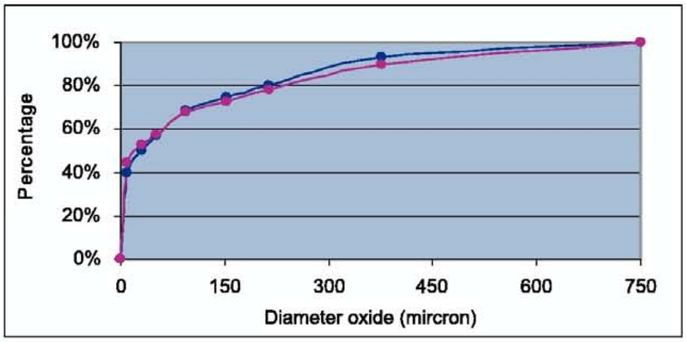

Figure 13.9: Particle size distribution Oxiton produced at ALSA, Hannover, Germany

NMC Density Table 13.12 shows density measurements of NMC-Residue (NMCR) from ALSA, the flux processing plant in Hannover, Germany. The density of wet NMCR is 1.92 g/cm^3. After drying, the density of the dry NMCR was found to be 2.92 g/cm^3. The dry NMCR was calcined at 750°C to convert hydroxides into oxides. The density of calcined NMCR was 3.22 g/cm^3. The NMCR from ALSA has a lower density then the NMC particles from the fluxes samples from KKM. Some experiments were done with NMC particles screened out of the flux. The density was sometimes even exceeding 3.5 g/cm^3. The densities of NMC particles from different size classes were even different. Some minerals are heavier or lighter than others and more likely to occur in a certain size class. Differences in density measurements can be caused by internal porosities, other chemical composition of the NMCR and the presence of very fine metal droplets.

Table 13.12: Density measurement of the NMCR from ALSA

Sample	Experiment number					Average
	1	2	3	4	5	(g/cm^3)
wet	1.98	1.83	1.83	1.94	2.00	1.92
dry	2.90	2.92	2.93	2.93	2.92	2.92
calcined	3.22	3.22	3.22	3.23	3.22	3.22

Particle size distribution of NMCR from ALSA According to figures from ALSA d_{50} of the NMC is 150 μm. However, the particle size distribution in Figure 13.9, as measured by the authors, indicates that the amount of small particles is higher; the average particle size, d_{50}, is 50 μm. This particle size distribution will be used for further calculations.

In each furnace cycle the NMC particle size distribution is different. The amount and size of the NMC particles in the flux are a result of the feed material properties i.e. when there are foils, UBC, etc. present in the feed material then it is likely that percentage of small NMC particles present in the flux is much higher.

Derivation of theoretical viscosity equations from experimental data Various relationships between viscosity and volume percentage of solids were described that might be applicable to the salt flux viscosity were presented previously. These relationships were fitted by least squares to the measured data and the respective parameters determined. The parameters K_1, K_2 and K_3, Eq. 13.11 becomes Eq. 13.18. The R^2 of Eq. 13.18 is 0.78 and therefore this equation is not likely to represent the true viscosity of the flux.

$$\frac{\mu_m}{\mu_0} = 1 + 2.71 \cdot 10^4 \cdot \Phi - 8.97 \cdot 10^5 \cdot \Phi^2 + 6.72 \cdot 10^6 \cdot \Phi^3 \tag{13.18}$$

Similarly least squares fitting estimates A and B in Eq. 13.12 hence producing Eq. 13.19, for which R^2 of Eq. 13.19 is 0.99 and hence high enough to assume this equation is able to represent the viscosity of the salt flux.

$$\frac{\mu_m}{\mu_0} = 1 + 2.5\Phi + 10.05\Phi^2 - 3.03 \cdot 10^{-7} e^{1.97 \cdot \Phi} \tag{13.19}$$

Least squares fitting estimates the parameters n and Φ_{max} Eq. 13.13, producing Eq. 13.20. The R^2 of Eq. 13.20 is 0.98, therefore the equation also gives a good indication of the viscosity of the flux. The value of Φ_{max}, which is 0.139, indicates that the flux starts to freeze when the amount of solids is 13.9 volume-%.

$$\frac{\mu_m}{\mu_0} = \left(\frac{\Phi}{0.139}\right) \cdot e^{2.5 + \left(\frac{\Phi}{0.139 - \Phi}\right)^{1.07}} \tag{13.20}$$

Eq. 13.21 is produced by the least-squares fitting of α and β in Eq. 13.14. The R^2 of Eq. 13.21 is 0.99. The value for α is 7.44 and the reciprocal value is 0.134, implying therefore that the maximum amount of NMC before the flux freezes, according to the Einstein-Roscoe equation is 13.4 volume-%.

$$\frac{\mu}{\mu_0} = (1 - 7.44 \cdot \Phi)^{-3.95} \tag{13.21}$$

Influence of particle size on flux viscosity To find out whether the flux viscosity is not only dependent on the volume percentage but also on the particle size of NMC particles, viscosity measurements were done with coarser NMC particles of 30 μm. The viscosities of two fluxes with same volume percentage NMC but with respectively particle sizes of 10 and 30 μm were compared. Due to the presence of more particles there is more interaction between the NMC particles in a flux with 10 μm particles. The number of particles with a diameter of 10 μm is 27 times higher ($\left(\frac{30}{10}\right)^3$ =27) than the number of particles with diameter of 30 μm in a distinct volume of liquid salt. It was visible that in the crucible with the coarser fraction the NMC particles started to settle. The viscosity of flux with 30 μm particles proved to be smaller than the viscosity of a flux with 10 μm particles (Figure 13.10).

13.2.5 Sedimentation of aluminium in the salt flux

Sedimentation of particles within the salt flux are of crucial importance to metal recovery within the furnace. Whether the particle settles fast from the salt flux, slow or not at all depends on various factors which include (i) medium density, (ii) medium viscosity, (iii) concentration of solid particles, (iv) particle density, (v) particle shape, (vi) particle size, and (vii) flow conditions. When the concentration of a suspension is high enough there is interaction between the particles. In this situation retarded settling takes place i.e. the sedimentation rate of the NMC particles will be less then the settling velocity of a particle under free settling conditions. A difference is made between suspensions of fine and of coarse particles [380]. In

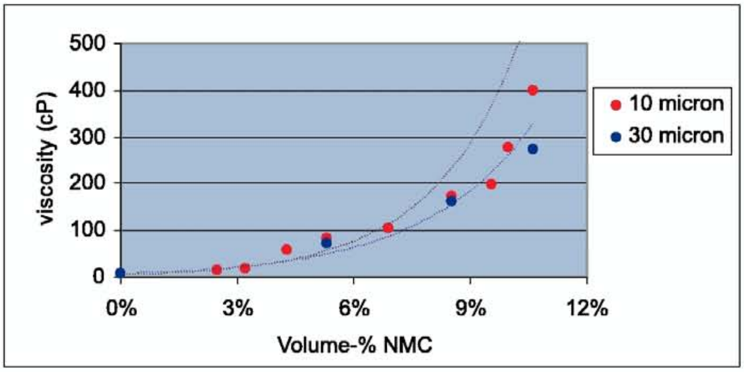

Figure 13.10: Influence of particle size of NMC on the salt flux viscosity

fine suspensions the fine solid particles influence the viscosity in contrast with coarse suspensions where the coarse particles settle. When there are a lot of fine particles in the suspension the viscosity increases and flocculation may take place when the fine particles flocculate, which can be significant as summarized in Table 13.13.

Table 13.13: Viscosity and/or sedimentation: (+) means positive effect and (-) means little effect

	Viscosity	Sedimentation
Fine suspensions, no flocculation	+	-
Fine suspensions, flocculation	+/-	+/-
Coarse suspensions	-	+

Sedimentation in fine suspensions

A concentrated suspension of fine particles may settle in two different ways. In the first the interface between clear liquid and the suspension moves downwards at a constant rate and a layer of sediment builds up at the bottom of the container or vessel. When this interface reaches the layer of sediment, the rate of fall of the interface decreases till there is a direct interface between the clear liquid and the sediment. Further consolidation takes place and liquid in the pores of the sediments is forced upwards. The second, less common, type of sedimentation in fine suspensions is obtained when the range of particle size is very great. There is no zone of constant composition and therefore there is no constant sedimentation rate. The main reasons for deviation of the sedimentation rate under hindered settling conditions in a concentrated suspension are:

- large particles settle faster then the small ones and therefore the effective density and viscosity of the fluid change,
- fluid at the bottom is displaces by particles and therefore there is an upward stream (the settling velocity is less then the actual velocity relative to the fluid),

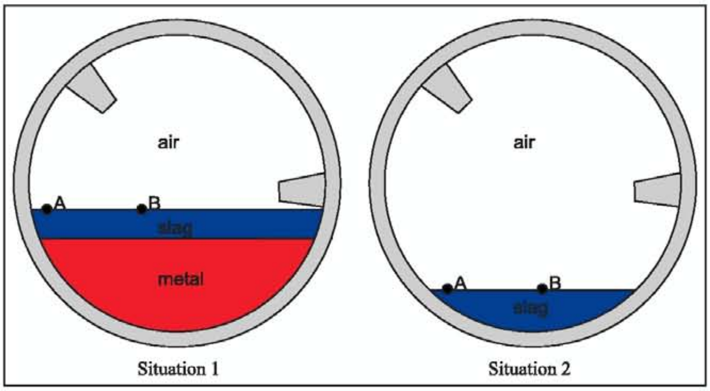

Figure 13.11: Salt flux layer before and after metal tap

- small particles tend to be dragged down by the motion of the large particles, and
- flocculation increases the effective size of small particles.

It is very difficult to predict the rate of sedimentation in a suspension of fine particles. The presence of an ionised fluid or the surface of the particle, influences the degree of flocculation. The size and density of these flocculants are different than the independent fine particles. Another factor influencing the sedimentation in fine suspension is agitation. The suspension must be gently stirred to get the highest consolidation rate possible. This principle is used in a thickener, where small particles fill the gaps between larger particles. Other factors that influence the sedimentation process are the shape and diameter of the vessel, the height of the suspension, and the volumetric concentration of particles. Some aspects about these factors and their role in the sedimentation of NMC particles in the salt flux will be described below.

Effect of vessel shape on sedimentation Walls of a vessel that face downwards have a considerable effect on the sedimentation e.g. sometimes even inclined plates are inserted in an inclined tank to accelerate the rate of settling. In Figure 13.11 the flux before and after metal tap is shown. In *Situation 1* the metal is still in the furnace and the flux layer is more or less a rectangular block, while in *Situation 2* the metal is tapped and the shape of the flux phase is completely different. In this case the furnace shape has a higher effect on the settling of NMC particles and Al droplets.

In *Situation 1* the NMC particles and Al droplets at point B will settle faster then in *Situation 2* (shorter depth), hence the particles at point A in *Situation 1* will settle slower then in *Situation 2* (higher depth).

Diameter of the vessel When the ratio between the particle diameter and the vessel diameter is greater than 100, the walls of the vessel have no effect on the sedimentation rate. Therefore the walls of the rotary furnace are not influencing the sedimentation of the NMC and Al particles ($d_{furnace}$=2500 mm; $d_{particle} = 10^{-3}$ to 1 mm).

Concentration of the suspension The higher the concentration the lower the rate of fall of the sludge line because more fluid is displaced and there is a higher upward velocity of this displaced fluid. The final consolidation of the sediment is the last and slowest part of the sedimentation process. The fluid in the sediment has to be forced upward and flow through small openings of the sediment. The lowest part of the sediment is the most consolidated due to the weight of the particles lying above.

Sedimentation in coarse suspensions

The particles in coarse suspensions are sufficiently large to neglect flocculation and their effect on viscosity. Calculating the settling velocity [381] of an isolated particle is not difficult. But normally particles that settle in a suspension have a lower settling velocity then their actual velocity to the fluid. This because of the up-trust of displaced fluid. The different forces acting on a settling particle are the gravity force, drag force and buoyancy force. A particle that has a higher density then the medium (which does not has an extremely high viscosity) will flow down and experience the various forces which are summarised in Eqs. 13.22 to 13.26.

$$F_{downwards} = F_{gravity} - F_{buoyancy} = \frac{\pi}{6} d^3 \cdot g \cdot (\rho_p - \rho_f) \tag{13.22}$$

Every object moving through a fluid or gas will undergo a drag force. The drag force is a function of diameter, density and velocity of the particle and of the friction factor, f. The friction factor or drag coefficient is depending on the flow regime around the particle and therefore depending on the Reynolds number, hence the upward drag force is given by Eq. 13.23.

$$F_{upwards} = F_{drag} = f \cdot \frac{\pi}{4} \cdot d^2 \cdot \frac{1}{2} \rho_p \cdot v^2 = f \frac{d^2 v^2 \rho_p \pi}{8} \tag{13.23}$$

Since the particle is not accelerating i.e. forces are at equilibrium, it follows that the terminal velocity is defined by Eq. 13.26.

$$F_{down} = F_{up} \tag{13.24}$$

$$\frac{\pi}{6} d^3 \cdot g \cdot (\rho_p - \rho_f) = f \frac{d^2 v^2 \rho_p \pi}{8} \tag{13.25}$$

$$v = \sqrt{\frac{d \cdot g(\rho_p - \rho_f)4}{f \cdot \rho_p \cdot 3}} \tag{13.26}$$

The friction factor is different for the various flow regions (i) for laminar flow Stokes law is used, (ii) for a Reynolds number between 2 and 500 the intermediate law has to be used, and (iii) when Reynolds number is higher then 500 there is a turbulent flow region and Newton's law is used to calculate the settling velocity. The friction factor for these three types of flow and therefore the equations for the settling velocity are different as given by Eqs. 13.27 to 13.31. The drag coefficient for NMC particles with various shapes will also be different. *(By substituting Eq. 13.27 into Eq. 13.26 the settling velocity becomes Eq. 13.28.)*

Stokes law: laminar flow ($\Re < 1$) When the particle is assumed to be spherical the drag coefficient is[2] given by Eq. 13.27.

$$f = \frac{24}{\Re} = \frac{24\mu}{\rho \cdot v \cdot d} \tag{13.27}$$

---

[2] $\Re$ – Reynolds number

$$v = \frac{d^2 g(\rho_p - \rho_f)}{18\mu} \tag{13.28}$$

Intermediate flow $(2 < \Re < 500)$ The drag coefficient is a function of the Reynolds number as shown by Eq. 13.29 and settling velocity is given by Eq. 13.30.

$$f = \frac{18.5}{\Re^{3/5}} \tag{13.29}$$

$$v = \left(\frac{d^{8/5} g(\rho_p - \rho_f)\rho_p^{-2/5}\mu^{-3/5}}{13.875}\right)^{5/7} \tag{13.30}$$

Newton's law $(500 < \Re < 2 \times 10^5)$ The drag coefficient is f=0.44 for this situation and hence the settling velocity is given by Eq. 13.31.

$$v = \sqrt{\frac{3.03 \cdot d \cdot g(\rho_p - \rho_f)}{\rho_p}} \tag{13.31}$$

Experimental estimation of the settling velocity

The settling velocity of a particle can be calculated by Eq. 13.28, Eq. 13.30 or Eq. 13.31. Which equation has to be used is dependent on the type of flow around the particle. When the settling velocity of a particle is calculated the first assumption that has to be made is that there is a laminar flow region around the particle. Then the settling velocity can be calculated with Eq. 13.28. The Reynolds number can be calculated to check whether the assumption of a laminar flow region around the particle was correct. When this Reynolds number is smaller than 1 the calculation and the assumption of laminar flow are correct. When the Reynolds number is higher then 1, there is no laminar flow but intermediate or turbulent flow. The settling velocity is again calculated but now with Eq. 13.30, assuming that there is intermediate flow. The Reynolds number for this settling velocity must be between 2 and 500. When the Reynolds number is higher then 500 the settling velocity should be calculated with Eq. 13.31, assuming that there is turbulent flow. In this way all velocities of different particle sizes can be calculated. Table 13.14 shows the settling velocity calculations of NMC particles in molten salt. The settling velocities of particles of 10, 30 and 52 μm are correct but the coarser particles have a Reynolds number bigger then 1. So the next step is to check whether these particles have a settling velocity following the intermediate law. When the Reynolds number is still exceeding 500 the settling velocity is calculated with Newton's law (like particles of 2500 μm and 5000μm). The calculations in Table 13.14 show that particles < 52 μm settle extremely slow or not at all. When the settling velocity of a particle is below 1 m/h it is assumed that the particle will never settle [367]. A particle of 21 μm has a settling velocity of exactly 1 m/h (0.28 mm/s). This would mean that particles coarser then 21 μm will settle in a certain time interval and that particles smaller then 21 μm will always remain suspended and effect the suspension viscosity.

Space between NMC particles The space between two particles assuming that there is no interaction between the particles is of the order 10μm (see calculation). It is obvious that with such a small distance between the particles interaction must occur! In spite of this a simplified sedimentation rate of the NMC particles in the salt flux is calculated later on in this section assuming that no interaction occurs.

Table 13.11: Calculation of settling velocity of different particles - partially validated by experiment

Stokes law (laminar flow, ℜ < 1)				Intermediate law (2< ℜ < 1)				Newton's law (500< ℜ < 2 × 10⁵)			
NMC		validity test		NMC		validity test		NMC		validity test	
d (μm)	v (m/s)	ℜ	check	d (μ m)	v (m/s)	ℜ	check	d (μ m)	v (m/s)	ℜ	check
5000	1.6E+01	212874	no	5000	5.8E-01	7701	no	5000	2.6E-01	3408	yes
2500	4.0E+00	26609	np	2500	2.6E-01	1711	no	2500	1.8E-01	1205	yes
750	3.6E-01	718	no	750	6.6E-02	132	yes	750	9.9E-02	198	no
375	9.0E-02	90	no	375	3.0E-02	30	yes	375	7.0E-02	70	no
215	3.0E-02	17	no	215	1.6E-02	9	yes	215	5.3E-02	30	no
153	1.5E-02	6	no	153	1.1E-02	4	yes	153	4.5E-02	18	no
94	5.7E-03	1.4	no	94	6.2E-03	2	yes	94	3.5E-02	9	no
52	1.7E-03	0.2	yes	52	3.1E-03	0.4	no	52	2.6E-02	4	no
30	5.8E-04	0.0	yes	30	1.7E-03	0.1	no	30	2.0E-02	2	no
10	6.4E-05	0.0	yes	10	4.8E-04	0.0	no	10	1.1E-02	0	no

Example 13.6

In order to picture what is happening inside the salt flux, it is possible to calculate the space between the NMC particles, neglecting flocculation. In order to find out whether the interaction between the particles is likely to occur, the space between 2 NMC particles is calculated i.e. x is the distance between the two particles from the surface of the one particle to the surface of the other particle, both of diameter $2r$. The average particle size according to the particle size distribution of the NMCR from ALSA (Figure 13.9) is about 50 μm. The weight-% of NMC is assumed to be 33.20% and the volume-% is 22.41%. The volume of 1 particle with a diameter of 50 μm is given by Eq. 13.32 and the number of NMC particles present in 1 m^3 of salt flux is given by Eq. 13.33.

$$V_{particle} = \frac{4}{3}\pi r^3 = \frac{4}{3}\pi(0.000025)^3 = 6.54 \cdot 10^{-14} \tag{13.32}$$

$$\frac{22.41 volume\text{-}\% \cdot 1m^3}{V_{particle}} \frac{0.2241m^3}{6.54 \cdot 10^{-14}m^3} = 3.42 \cdot 10^{12} \ \ particles \tag{13.33}$$

The amount of particles on one of the axes of a cube of 1 m^3 is given by Eq. 13.34.

$$\sqrt[3]{3.42 \cdot ^{12}} = 15072 \ \ particles \tag{13.34}$$

Therefore between 2 particles of 50 micron there is a space (x) of x as defined by Eq. 13.35.

$$x = \left(\frac{1}{15072}\right) \cdot 10^6 - 50 = 64 - 50 = 14 \ \ \mu m \tag{13.35}$$

Sedimentation within the rotary furnace The rotary furnace sampled has an inside length of 5.07 meters and an outside diameter of 3.65 meters. During the melting process the furnace is normally rotating with a speed of 3 rpm. So the 6 paddles dive into the flux phase (as Figure 13.12 shows) with a speed of 3 rpm. The inside diameter of the furnace is 2.7 meters. The circumference is $2\pi r = 8.5$ meters. The speed of the paddles is 3 rpm = 25 meters/minute = 0.42 m/s. This speed is higher then the settling velocity of the biggest NMC particle and the biggest aluminium droplet in the flux. Therefore these NMC particles and aluminium droplets will be notoriously stirred up by paddles and kept suspended. When the flux leaves the trajectory it starts to counter act and fall back on the flux phase and causes turbulence and mixing.

The sedimentation of NMC particles and aluminium droplets can be explained as follows: (i) At t=0 the furnace stops rotating at which time the NMC particles are now still homogeneously mixed in the salt. (ii) At $t = x$ the particles are settling, the big particles settle faster and reach the bottom of the flux phase first. (iii) At $t = \infty$ a layer of NMC is formed that blocks the aluminium droplets, therefore these aluminium droplets will never reach the metal phase and remain entrapped.

Calculations of sedimentation velocity in the flux phase Using the above insights the settling velocity of the different NMC particles and the time it takes to form a sediment layer the flux phase can be calculated. This is done by arbitrarily dividing the salt layer into 10 layers, each having at t=0 the same volume concentration and particle size distribution of solids. Before the metal tap (situation 1 of Figure 13.11) the flux layer can be assumed to

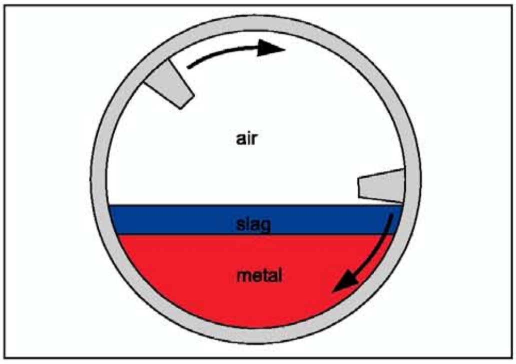

Figure 13.12: Paddles diving into the flux and dragging material under salt flux

approximate a rectangular block. The area of interface between metal and flux is about 8 m^2 and the height of the flux phase is assumed to be 20 cm, therefore the total volume of the flux phase is then 1.6 m^3. In each of the 2 cm slices, the NMC particles are divided into different particle sizes of respectively 750, 375, 215, 153, 94, 52, 30 and 10 μm according to the particle size distribution of Figure 13.9. The settling velocity the particles can be calculated with Stokes and/or the intermediate law (see Section 13.2.5). A particle of 750 μm settles first and particles of 30 μm only after a much longer period of time, especially the small particles from the upper layer will may be never reach the consolidated layer. These very small particles also contribute to the viscosity increments. To simplify the model of the sedimentation of NMC particles in the flux phase the following assumptions were made:

- The density of salt = 1.67 g/cm^3, this is the mean value of theoretical and experimental densities. The density of NMC = 3.00 g/cm^3
- The viscosity of salt with 9.5 volume-% 10 μm NMC particles is 200 cP
- There is no interaction between the NMC particles and no coalescence takes place (there are free settling conditions)
- The flux phase is a rectangular block with a volume of 1.6 m^3 (height is 20 cm and surface of the bottom is 8 m^2 that can be divided into 10 layers with same properties, i.e. particle size distribution of NMC, NMC/Salt ratio, and temperature.

The graphs in Figure 13.13 and Figure 13.14[3] represent the thickness of the sediment layer formed versus the time that the furnace is not rotating. At t=0 the furnace stops rotating and the settling process starts. In order to calculate how much aluminium is still left in the flux after a certain time period, it is assumed that a thickness of 1.5 cm is enough to block the metal phase. This sediment layer is formed after 30 minutes when a porosity of 0% is assumed. Figure 13.15 shows the settling velocity of NMC particles of a certain size class versus their settling time e.g. a particle of 750 μm from the top layer 1 reaches the bottom layer 10 faster then a particle of 375 μm from layer 8.

As Figure 13.16 depicts that an aluminium droplet and NMC particle of same size will not settle simultaneously, the NMC particles have a higher density and will settle faster. However,

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[3] 40%, 20% and 0% refer to the porosity of the sediment layer.

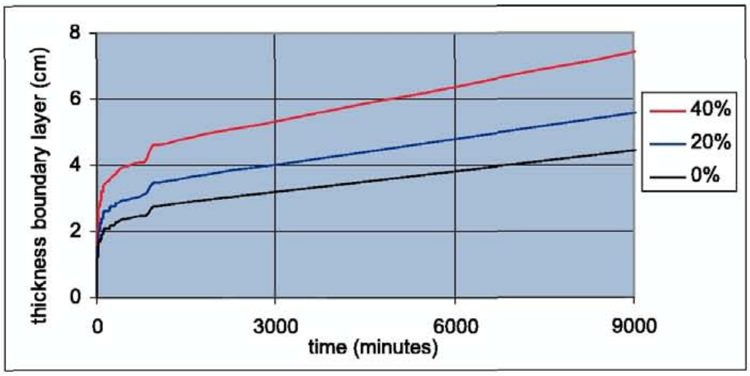

Figure 13.13: Thickness of NMC layer versus time

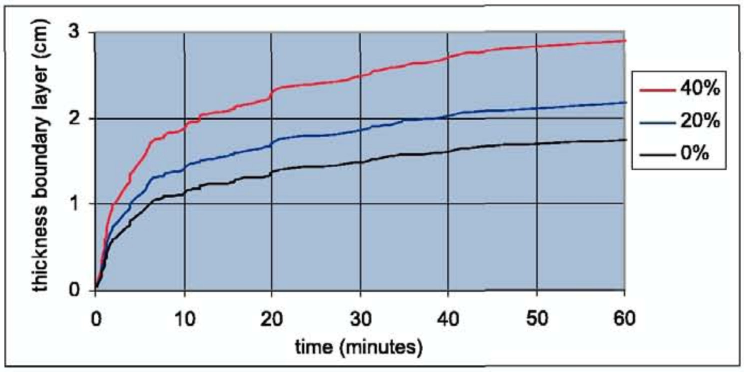

Figure 13.14: Thickness of NMC layer in the first hour

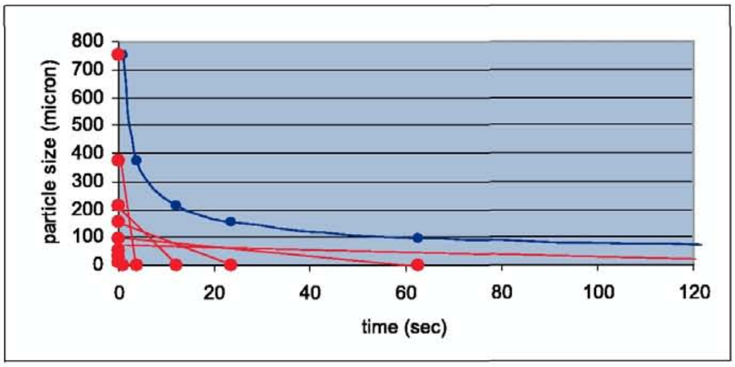

Figure 13.15: Particle versus settling time

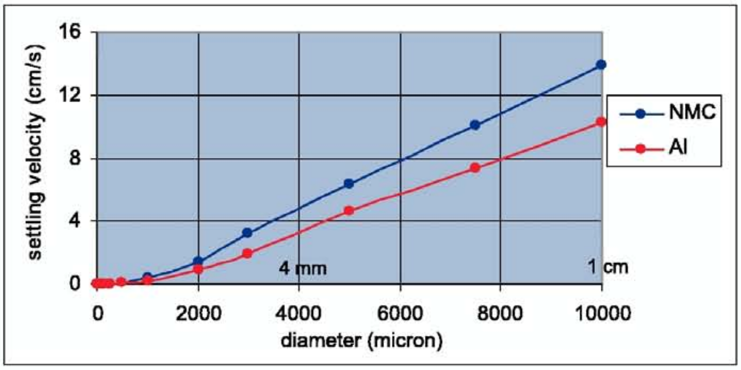

Figure 13.16: Settling velocities of the same sized NMC particles and Al droplets - NMC settles faster

big aluminium droplets settle much faster then small NMC particles. Therefore the chance that a big aluminium droplet at the bottom of the flux phase flows down to the molten metal phase before a blocking sediment layer is formed by NMC particles is high.

Summary

- **How much metal is entrapped in the salt flux?** The amount of metal entrapped in the fluxes was measured at average 4.6 mass-%. Some parts of the flux contain only 0.5 mass-% aluminium and others 18.5 mass-%.
- **Is the aluminium entrapped in the flux caused by the viscosity of the flux?** It is shown that there is no relation between the amount of aluminium entrapped in the flux and the NMC/Salt ratio in the flux samples from KKM. However, there is a relationship between the aluminium entrapped and the NMC particles smaller then 21 μm. These NMC particles are small enough to remain suspended and increase the viscosity of the salt flux that influences the settling velocity of the aluminium droplets. Therefore the relationship between aluminium droplets and fine NMC particles is given by Eq. 13.36.

$$\text{Settling velocity of Al droplets} = f(\mu) = f(NMC_{\leq 21\mu m}) \tag{13.36}$$

- **Is the viscosity of the flux depending on particle size and shape of the NMC particles?** The viscosity of a flux is not influenced by all NMC particles. About 60% of the particles are too coarse to contribute to viscosity increments and will settle after a certain time interval. The viscosity influences the settling velocity of these coarser NMC particles. Therefore the relation between coarse and fine NMC particles is given by Eq. 13.37.

$$\text{Settling velocity of } NMC_{>21\mu m} = f(\mu) = f(NMC_{\leq 21\mu m}) \tag{13.37}$$

The viscosity of the flux is incremented by NMC particles smaller then 21 μm. It is shown that there is a linear increase of the viscosity until a certain critical volume percentage (of particles with an average particle size of 10 μm) is reached and then the viscosity starts to increase exponentially. The viscosity is certainly depending on the shape of the particles. NMC particles have various different sizes and are surely not spherical. These asymmetrical shaped NMC particles are more likely to interact with each other then spherical particles.

- **What function describes the viscosity of a salt flux?** NMC particles with a diameter smaller than 21 μm will never settle in liquid salt. The relation between volume percentages of NMC particles with an average particle size of 10 μm and the flux viscosity is crucial. The flux viscosity measured with the high temperature viscometer fit with a R^2-value of 0.99 in respectively Eq. 13.19 and Eq. 13.21.
- **Salt flux: a flux or high temperature slurry?** Molten salt flux is in fact a high temperature slurry. About 40% of the NMC particles are fine enough to remain suspended in the flux but the coarser particles settle when the furnace is not rotating. When the furnace stops rotating NMC particles and aluminium droplets start to settle. The NMC particles form a sediment layer that blocks aluminium droplets reaching the interface later to flow further down to the metal phase. A sediment layer with 0% porosity of 1.5 cm is already formed after 30 minutes. Then aluminium still left in the flux lost the settling race from NMC particles.
- **Aluminium entrapped in the flux?** There are some reasons for aluminium to be present in the flux. Aluminium can be enclosed by salt and oxides and then end up in the flux phase. During the rotation of the furnace the flux phase is concerning the NMC content a more or less homogeneous bath. This means that the NMC particles are kept in the flux due to a stirring force. So when the furnace is rotating the NMC particles have no chance to form a sediment layer. The aluminium droplets undergo the same forces and have no chance to settle to the metal phase. The paddles also lift liquid aluminium from the metal phase into the flux phase where they form small droplets.

At least one conclusion of this work is the re-definition of a practical salt factor: The salt factor represents the amount of salt necessary to keep the content of NMC particles < 20 μm in the salt flux (HTS) below 9.5 vol.%.

13.2.6 Processing of salt flux

The salt flux carries up to 10 wt.% of valuable aluminium cast alloys and more than 97% of the melting flux. In the 70's first attempts were made to process the salt flux to regain metal and salt. Due to the combined attack of abrasion and corrosion the selection of appropriate material for leaching and crystallization equipment proved to be decisive for a breakthrough in salt flux processing. By the mid 80's these problems were solved and large scale operations built in Germany, Italy, France, Norway and Spain to handle almost all of the salt flux generated in continental Europe. The fundamental processing steps of the various salt flux processing plants are identical:

- separation of entrapped metal by dry or wet crushing and milling and screening,
- leaching the fines with hot water, generating a rather saturated brine,
- handling of the gasses developed during leaching by incineration or scrubbing,

- solid-liquid separation and washing of the solid residue (NMC) to <0.5 wt.% soluble chlorides,
- crystallization of the salt by multi-stage vacuum or vapour compression (closed systems) or flash evaporation (open systems),
- blending the crystallized salt to melting flux (adding KCl, fluorides, drying, etc.), and
- multiple turn around of filtered NMC to kill residual metal by contact with air.

The gasses developed when the salt flux fines are leached with water consist of *(these compounds are responsible for the large quantity of gas development when salt flux comes into contact with water: 7.5* m^3 CH_4*, 2.8* m^3 NH_3 *and 0.1* m^3 PH_3*/t salt flux, the latter one of particular toxicity)*:

- CH_4 from Al_4C_3 (source organic material in scrap)
- NH_3 from AlN and Mg_3N_2 (source nitrogen purging or dross burn)
- PH_3 from AlP (source P-treatment or phosphate layers on foils and sheet)
- H_2 from aluminium metal
- H_2S from Al_2S_3 (source from sulphur in fuel).

Typical hydrolysis reaction are:

$$Al_4C_3 + 12H_2O \rightarrow 4Al(OH)_3 + 3CH_4(g) \tag{13.38}$$

$$AlN + 3H_2O \rightarrow Al(OH)_3 + NH_3(g) \tag{13.39}$$

$$AlP + 3H_2O \rightarrow Al(OH)_3 + PH_3(g) \tag{13.40}$$

$$Al_2S_3 + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2S(g) \tag{13.41}$$

Hydrogen and methane require particular attention regarding the explosion concentration of the off-gas (air with > 4 vol.% H_2 + CH_4 is explosive). Ammonia is usually converted into ammonia-sulphate and delivered to the fertilizer industry. Garlic smelling (minimal warning smell conc. 0.02-3 volume ppm PH_3) phosphine is extremely toxic (1500 vol. ppm inhaled over 10 minutes is lethal). It is always contaminated by P_2H_4, which is unstable and decomposes into PH_3 and amorphous white phosphorus when in contact with light. This reaction and the subsequent oxidation of elemental phosphorous cause of the notorious little fulminates whenever freshly filtered NMC piles come into contact with air, e.g. by charging with front-loaders. The characteristic stench of combined ammonia and phosphine is a specific feature of salt flux produced from secondary aluminium smelting. A cost saving and effective combination of milling and leaching has recently been integrated in one of the German salt flux processing plants: wet milling of pre-crushed salt flux by addition of cold water, which reacts very slowly with aluminium metal therefore producing rather low gas emissions. After wet screening the leaching is carried out at elevated temperatures to promote the hydrolysis reactions of the various aluminium compounds with water. A typical average mass balance of a salt flux processing plant is shown in Table 13.15.

The salt content of the NMC residue requires an addition of 1 kg make-up salt/t salt flux. The total loss of water (in gasses and moisture of the NMC residue) needs to be compensated for by about 250 kg of make-up water/t salt flux. Washing of NMC residue is one of

Table 13.15: Typical average mass balance of a salt flux processing plant

(Dry kg/t salt flux)	Total	Metal	NMC	Salt
Salt flux	1000	85	325	590
Metal granulate	81	65	8	8
Salt	581	0	0	581
NMC	348	0	347	1
Subtotal	1010	65	355	590

the crucial aspects of salt flux processing. The NMC residue is used by the cement industry as a replacement for bauxite (for those which have a Al_2O_3 deficit in their feed) or mineral fibre producers. In both the applications a content of <0.2 wt.% of soluble chlorides are required. In order to attain such a low content requires intensive washing, i.e. a huge surplus of wash water. However, in closed systems only the condensate from crystallization is available. This volume can only be increased by reducing the salt concentration in the produced brine, which immediately results in an increased energy demand for water evaporation. The technical solution is the installation of multi-stage counter-current decantation systems; a 4-stage CCD system allows the 0.2% target salt concentration in NMC to be achieved, even when crystallizing saturated brine (360 g salt/l brine).

The total outlet of NMC in Europe (separated from salt flux) is momentarily about 390 000 dry metric ton/a. This tonnage corresponds to 205 000 t aluminium/a i.e. in Europe ca. 205 000 t aluminium metal is irreversibly converted into oxide, which is equivalent to 2.5% of Europe's aluminium consumption!

The average magnesium content in cast alloys is about 0.25 wt.%. Due to its higher oxidation rate than aluminium during scrap melting and refining the average MgO content of NMC is 7.8 wt.% instead of 0.3 wt.%, if it is oxidized proportionally to its alloy content. The amount of such oxidised magnesium is consequently 390 000 × (0.078 - 0.003)/1.66 = 29 000 t magnesium metal/a. This tonnage has to be fed back into the aluminium alloy utilization cycle as magnesium metal, just to compensate for the over-proportional magnesium losses (relative to the aluminium metal losses) that occur. The 29 000 magnesium t/a correspond to approximately 65% of the total European magnesium consumption in the aluminium alloy sector. Aluminium is a major alloying element of magnesium die-casting alloys and magnesium is a minor but important alloying element of aluminium wrought alloys (e.g. beverage cans). Therefore analyses of one of the recycling systems needs to consider the interrelation between both the light metals as depicted by Figure 13.17.

Processing costs of salt flux

Salt flux from aluminium scrap melting contain 8-10 wt.% of entrapped metal droplets and 45-65 wt.% of recyclable flux and possibly dioxines [4]. Constituents such as nitrides, phosphides and sulphides generate noxious gases when they come in contact with water (or even with air moisture). A recycling charge would be about 70 €/t, sales proceeds from metal plus flux about 120 €/t. A reasonable throughput capacity for a salt flux recycling plant would be 60 000 t/a. A capital investment for a plant using best available technology can hardly be less than 25 million €. The total revenues would then be 190×60 000 = 11.4 million €/a, the minimum required return of investment would sum up to 4.7 million €/a, leaving a span for total operating cost of 6.7 million €/a, equivalent to 111 €/t of salt flux. This is realistic: 50

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[4] Cyclic carbo-chloride compounds

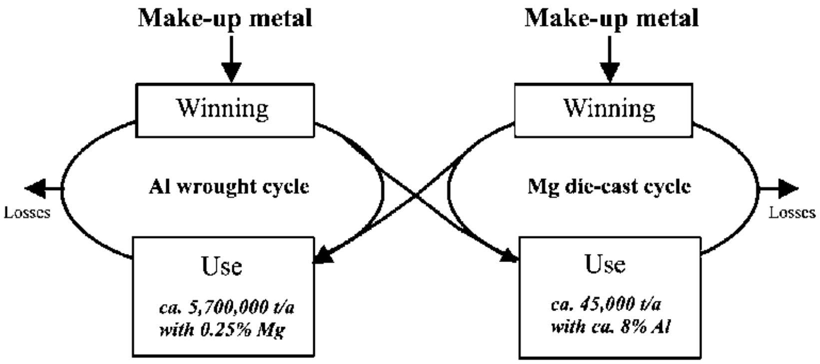


Figure 13.17: Interrelation between the Al and Mg cycles (data for 2000)

people may be needed to run such plant at cost of about 40 €/t; steam for crystallisation of salt will cost about 7 €/t and repair and maintenance cost (abrasive and corrosive media) will be approx. 4% of total investment or 17 €/t. The remaining 47 €/t are seemingly sufficient to cover all other cost (including administration).
Consequence: A throughput capacity of 60 000 t of salt flux seems to produce adequate profit. As 1 t of recycled aluminium scrap will generate about 0.4 ton of salt flux, the envisaged throughput capacity corresponds to an aluminium melting capacity of roughly 150 000 ton scrap/a. In Central Europe this capacity can be found in many industrialised areas of about 200 km radius. This distance allows transportation of salt flux to a central recycling plant at reasonable cost of about 7 €/ton flux. This amount comes on top of the recycling charge, i.e. the aluminium scrap melter will have to pay to the salt flux processing plant in total a treatment or recycling charge of 77 €/t of recycled salt flux.

13.2.7 Melting of some modern aluminium materials

In order to determine the effect of design choices, shredding and material quality on the recycling of cars, the secondary recovery of aluminium from new aluminium applications, such as hybrids, sandwich structures and aluminium foams, related to their specific characteristics are discussed through melting experiments. Moreover the experiments provide data for the calibration of the developed optimization model e.g. on the relationship between the composition of the input of metallurgical processes and the final metal yield either caused by design or imperfect liberation or imperfect mechanical separation. Various types of aluminium applications, such as hybrids (glare and hylite), aluminium foams and sandwich structures were melted under controlled conditions to determine the metal recovery. The influence of (undesired) material combinations, foaming agents (air, TiH_2, etc.), additives (e.g. Al_2O_3, SiC), density of the foam, adhesives and structure of the material on final metal recovery are investigated by these experiments. Moreover the effect of melting temperature and salt flux composition for melting is investigated for the various aluminium applications to optimise metallurgical recovery. Xiao [352] characterized and melted various aluminium scraps under different experimental conditions, including rolling mill cuttings, cast ingots, margarine foils, bottle caps.

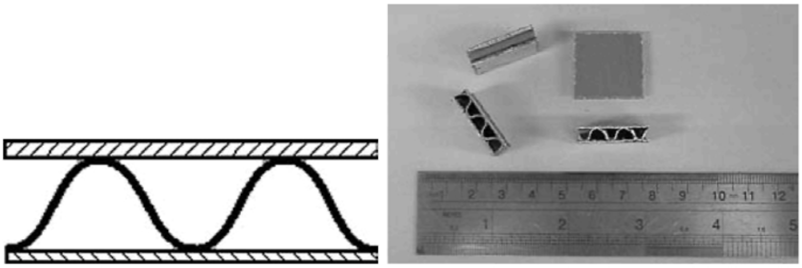

(a) (b)

Figure 13.18: (a) AlSi9 cast alloy; (b) the flux/metal after melting - ca. 100% metal recovery/yield is achieved from an ingot

Experimental

The recyclability of three types of aluminium sandwich applications, two hybrid materials, and three different aluminium foams have been experimentally studied. The experiments were carried out in a high temperature Carbolite chamber furnace equipped with a removable stainless steel retort for atmosphere control (Xiao [352]). The temperature was controlled to an accuracy of 5°C. After the crucible was charged and put into the furnace, the system was closed, and nitrogen gas was flushed through to protect the system from oxidation (however, note that aluminium nitride could be formed in very low quantities). The gas flow rate was controlled as 2 l/min. Alumina crucibles were used in the experiments. The scrap was melted in an alumna crucible at 800°C and 900°C with salt flux protection. Sufficient amount of salt was added to cover the scrap from oxidation and to adsorb the contaminants from the scrap. To ensure a good fluidity of the molten flux, a weight ratio of salt to scrap was controlled to be 5 in order to completely cover the scrap with the salt flux (the normal weight ratio of salt to scrap used in industry is 2). The NaCl-KCl ($-Na_3AlF_6$) system was used as salt flux for protecting metal from oxidation; absorbing contaminants; and promoting coalescence of aluminium droplets. After melting, the crucibles with the samples were cooled, washed with water, and the metal beads and the precipitates were filtered, dried and sieved at 0.25 mm. The filtered precipitates were prepared for XRF and XRD analysis. The fraction of metal recovered with respect to the total scrap (the metal yield) was calculated. The composition of the metal beads was analysed with an electron-microprobe (EMP) . This can be compared to the specifications of the input material (aluminium application). No stirring was applied. This was to bench mark against other experiments.

Mass balance and bench mark A mass balance was attained in the melting experiments, based on expertise built up over many bench marking experiments for various scrap types Xiao [352, 318]. A well-calibrated method was developed to establish a good mass balance for all in- and outputs, including the non-metal content (NMC) in the salt flux, flue dust, etc. To better compare the experimental results, AlSi9 alloy was melted in a previous study to establish a "bench mark", for which a 100% metal yield and recovery have been calculated under similar experimental conditions. The AlSi9 alloy and the sample after melting are illustrated in Figure 13.18.



(a) (b)

Figure 13.19: Sandwich A (a) structure; (b) picture of material

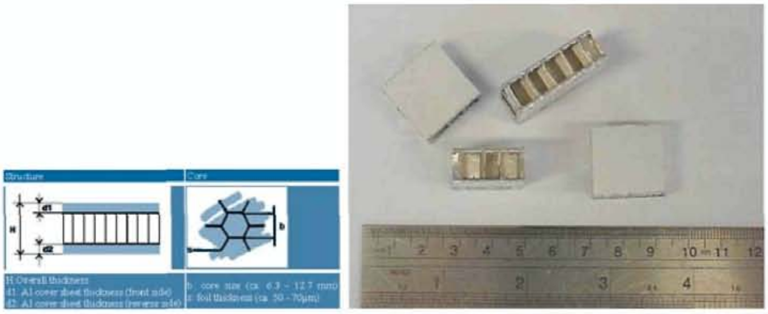
Salt flux The salt flux for these experiments contains 70 wt% NaCl - 30 wt% KCl without cryolite (Na_3AlF_6). Additional experiments were carried out containing 15 wt% cryolite in the salt flux, 85% forming the salt flux with the same ratio as mentioned above. The salt composition was selected based on the preferred European melt salt composition, considering that KCl is more expensive than NaCl. Theoretically the salt flux on equimolar NaCl - KCl composition (i.e. 44wt% NaCl - 56wt% KCl) would give better melting results, which corresponds to the eutectic temperature of about 650°C. Addition of cryolite to the mixture of NaCl and KCl is used to increase the interfacial tension between the salt and the molten metal, enhance the stripping of oxide film from metal droplets, favour the agglomeration of the metal drops and reduce the aluminium loss by entrapped metal into salt flux.

Sample preparation The different aluminium applications all coming from sheets have been cut into pieces of equal size (approximately 2cm x 2-4cm) in order to fit into the melting crucible. For the foam the closed metal pores are partially exposed to air due to this size reduction, which could have led to the oxidation of the created surface of the foam melting samples. However, in comparing the results for the different foam types, this will be of no influence, since the same procedure (cutting and melting) was applied to all materials.

New automotive aluminium applications

Hybrids Two different types of aluminium hybrids are investigated: Glare and Hylite. Glare is a fibre-metal laminate, consisting of 0.3 - 0.5 mm layers of aluminium and 0.3 - 0.45 mm layers of unidirectional glass fibre. The orientation of the glass fibre layers can influence the properties of the material. The main advantage of Glare over normal aluminium sheet is a large increase in fatigue strength at a reduced weight. Hylite consists of a polypropylene layer covered with two aluminium sheets, typically of 0.2 mm thick. For this project two variants of Hylite are tested: Hylite 1.2 (0.8 mm polypropylene) and Hylite 2.0 (1.6 mm polypropylene).

Sandwich panels Three types of aluminium sandwich applications were investigated. Figure 13.19(a) shows the structure of the Sandwich A, which is a metal sandwich panel in which two metal cover sheets are connected by a corrugated metal sheet. Figure 13.19(b) shows a picture of the material. The aluminium Sandwich A product consists of aluminium sheets of varying thicknesses, surface coatings and textures. The Sandwich A material tested is AlMg1 (EN AW-5005 H18) with a coversheet thickness of 0.3 mm (top and bottom), 5 m satin silver finish (eloxiert, 5 m Naturton).



(a) (b)

Figure 13.20: (a) Structure of Sandwich B and C; (b) picture aluminium honeycomb core

(a) (b) (c)

Figure 13.21: Aluminium foams: (a) Alporas; (b) Alulight; (c) Cymat

Figure 13.20 shows the structure of the Sandwich B and C material. Sandwich B and C is a composite panel consisting of two aluminium cover sheets in Peraluman-100, EN AW-5005 (AlMg1) with an aluminium honeycomb core. Sandwich B and C is produced with several core and cover sheet thicknesses. The material tested in these experiments are two types of composite panel, both with a coversheet thickness d1 of 1.00 mm for the front side and d2 of 0.50 mm for the reverse side, and a overall thickness H of 6 mm (Sandwich B) and 10 mm (Sandwich C) respectively. Figure 13.20 shows a picture of the material. The surface of both the front and reverse side cover is platinum white.

Aluminium foams Three different types of aluminium foams are considered and melted in order to investigate the influence of foaming gas, aluminium alloy and additives on the metal yield. Of each of the foam types, two different densities have been melted to determine the effect of density (or volume/mass ratio) on the metal yield. The foam types investigated and their characteristics are listed in Table 13.16 and depicted by Figure 13.21. In order to investigate the influence of the structural application (e.g. gluing) of aluminium foams the three different foam types being glued to wrought aluminium sheets are being melted under the same melting conditions as described. The effect of two different glue types was studied in order to determine the influence of different methods of joining aluminium foam to wrought aluminium sheets on the metal yield/recovery.

Table 13.16: Foam types investigated and their individual characteristics

Material	Relative density (%)	Foaming gas	Additives	Al Alloy
Alporas high	12.1	H_2	1.4%Ca, 1.4%Ti, 0.3%Fe, 0.007%Mg	
Alporas low	7.2	H_2	1.4%Ca, 1.4%Ti, 0.3%Fe, 0.007%Mg	
Alulight high	13.9	H_2	Al_2O_3, Ti, TiH_2	6xxx alloy
Alulight low	10.2	H_2	Al_2O_3, Ti, TiH_2	6xxx alloy
Cymat high	19.8	H_2	SiC (10-20%), Al_2O_3	A356
Cymat low	10.7	H_2	SiC (10-20%), Al_2O_3	A356

(a) (b)

Figure 13.22: Glare after melting, (a) metal phase and (b) salt flux

(a) (b)

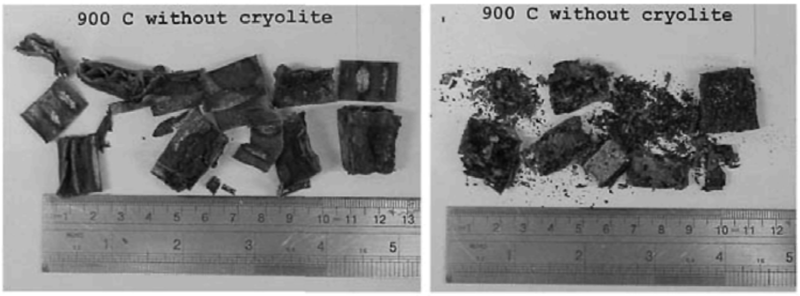
Figure 13.23: Hylite after melting, with (a) metal phase and (b) salt flux

Melting results

Three different hybrid aluminium applications (Glare, Hylite 1.2, Hylite 2.0), three aluminium applications(Sandwich A, Sandwich B and Sandwich C) and three aluminium foam applications, Alporas, Alulight and Cymat (all three for both high and low density) are melted under the conditions as described in the previous paragraph to determine the metal yield. In addition the effect of cryolite addition on the melting behaviour is investigated.

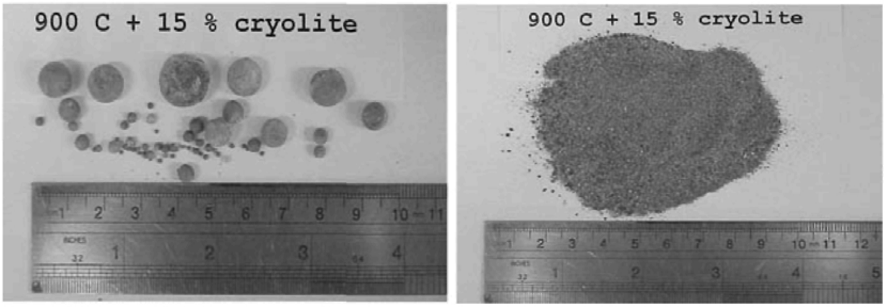
Melting results of aluminium hybrids The metal and salt flux phase after melting are illustrated by Figures 13.22 for Glare and by Figure 13.23 for Hylite.

Melting of aluminium sandwich panels Figure 13.24 clearly illustrates that no metal is recovered from the different sandwich panel types when melting under normal melting conditions without the addition of cryolite to the flux. The structure of the input material is still present in the material after melting, which is covered by a thin black layer, being the pyrolysed adhesive. It can be concluded from these experiments that both the Sandwich A material as well as the Sandwich B and C material cannot simply be charged to a melting



(a) (b)

Figure 13.24: (a) Sandwich A after melting, (b) Sandwich B and C after melting



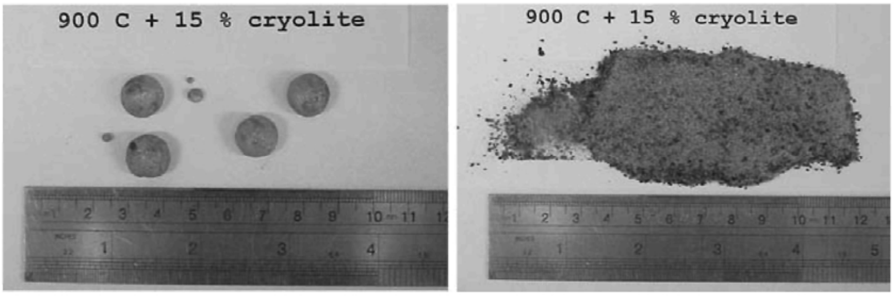
(a) (b)

Figure 13.25: Sandwich A; (a) recovered metal beads (b) salt flux after melting (15 wt% cryolite)

furnace without addition of cryolite, since no metal will be recovered this way. The Sandwich A and Sandwich B and C scrap are melted under the salt flux at both 800°C and 900°C, without cryolite. The results of the melting experiments at 900°C are shown.

It becomes clear from Figures 13.25 and 13.26 that metal can be recovered from the aluminium sandwich applications, when cryolite is added to the salt flux. It proves that cryolite addition has positive effect on the metal coalescence, when comparing the results to Figure 13.24. In general, higher concentration of cryolite in the salt flux gives better coalescence of the metal droplets. However cryolite addition at the same time increases the density of the salt flux, thus reducing the density difference between the salt and the metal. This in turn negatively affects the metal separation from the salt, and therefore the metal settling and coalescing.

Melting of aluminium foams The experimental results for the different foam types after melting under a salt flux without cryolite at 900°C are shown in Figures 13.27(a) to (f). These Figures clearly illustrate that it is difficult to recover metal from the different foam types when melting under normal melting conditions without the addition of cryolite to the flux. The structure of the input material is (partially) still present in the material after melting. It can be concluded from these experiments that the different metal foams as investigated here



(a) (b)

Figure 13.26: Sandwich B and C; (a) recovered metal beads (b) salt flux after melting (15 wt% cryolite)

cannot simply be charged to a melting furnace without addition of cryolite, since no good metal quality will be recovered this way. The results for the Alporas, Alulight and Cymat foams which are melted with addition of cryolite to the salt flux are illustrated for Cymat high and low density by Figure 13.28. The figures show the recovered metal beads as well as the residue from the salt flux. The salt flux precipitate is a residue (waste stream) of the melting operation. Materials present in this precipitate will be lost (this includes the irrecoverable cryolite). It becomes clear from Figure 13.28 that metal can be recovered from the different foam types, when adding cryolite to the salt flux. It proves that cryolite addition has positive effect on the metal coalescence, when comparing the results of Figure 13.27.

Metal yield

The experiments show the effect of material choices, material connections and combinations, construction of the material, the use of additives and foaming agents in foaming and specific material properties of new aluminium applications on the final metal yield/recovery. It is well known from previous studies that the oxide layer on the aluminium scrap decreases the metal yield during secondary aluminium recovery. The losses during melting due to irrecoverable aluminium oxide on the surface of the scrap are determined by the thickness of the oxide film. The oxide layer relative to the amount of aluminium is also influenced by the design of the material, which determines the surface to mass ratio of the aluminium application (high surface to mass ratios will often lead to a high amount of aluminium oxide present on the scrap). The density (pore surface) of the foam as well as the foaming gas used will determine the degree of oxidation of the surface of the aluminium foams. The use of irrecoverable alumina as additive/stabiliser in the foam will lead to a decrease in the metal yield. Previous research has shown the decrease of metal yield due to the presence of organic components in the aluminium application/scrap, which could be caused by the use of organic components such as the epoxy/fibre layer for the glare and the polypropylene layer of the Hylite, as well as the use of adhesive in the structure of the sandwich applications and in the application of foams. In general, it is shown that the design (material combinations, construction, additives, etc.) and production of these new aluminium applications have significant effect on the melting behaviour. Without addition of cryolite, low quality metal was recovered from the scrap. This implies that these types of material cannot simply be charged to a melting furnace for metal recovery. The various yields and recoveries are summarised in Table 13.17.

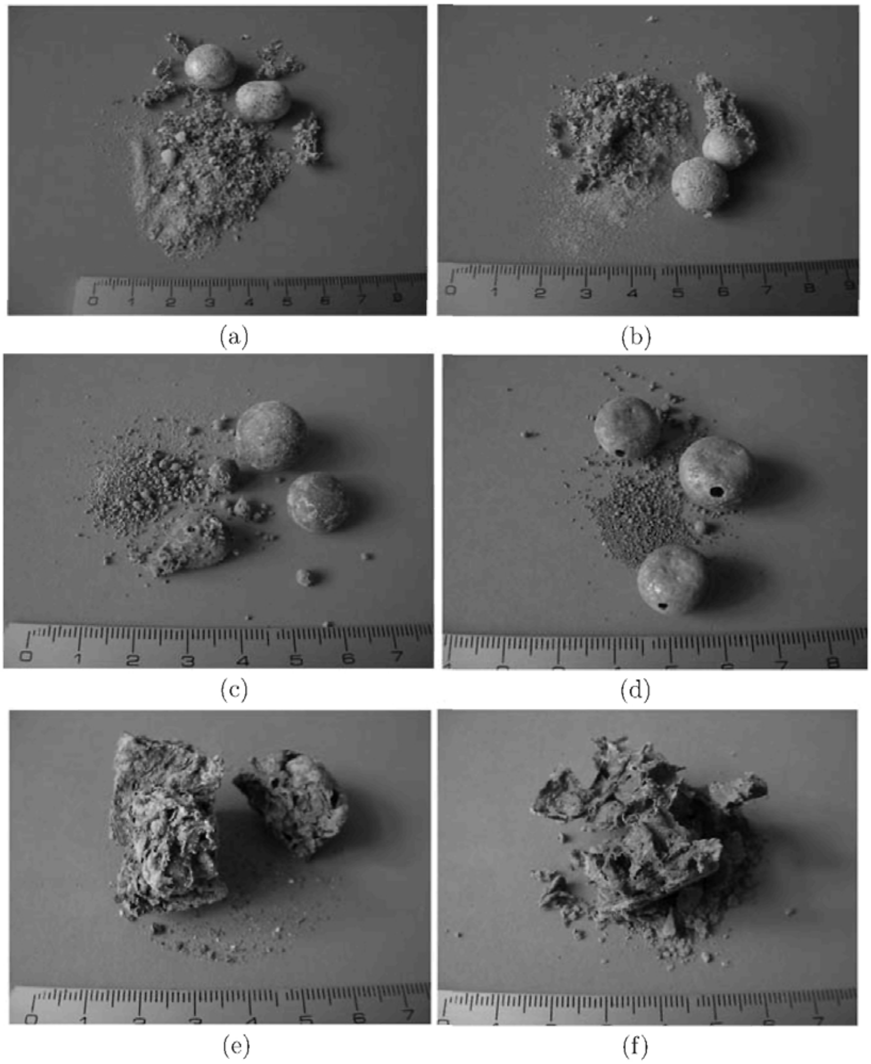
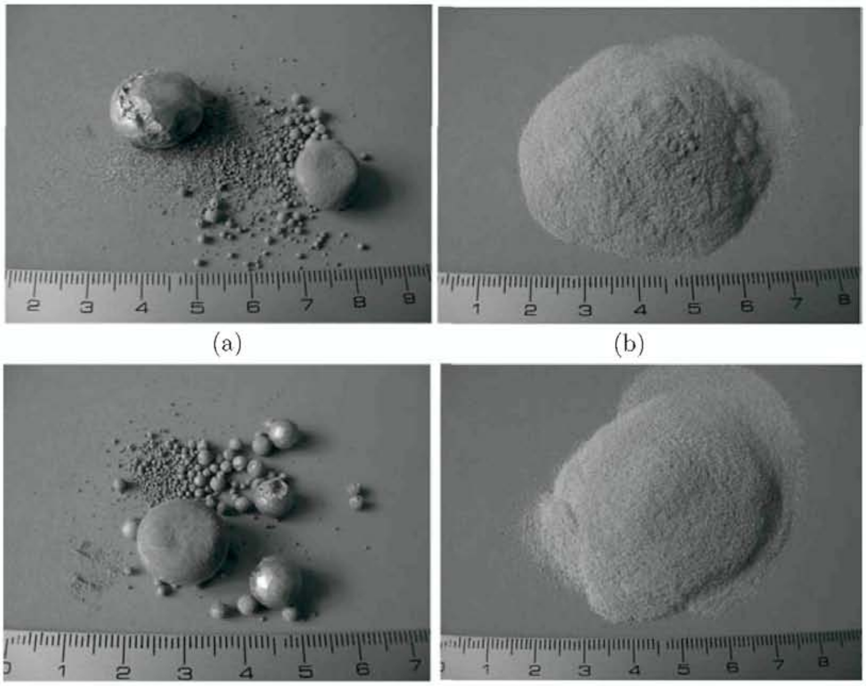


Figure 13.27: Aluminium foams after melting without cryolite; (a) Alporas high (b) Alporas low (c) Alulight high (d) Alulight low (e) Cymat high (f) Cymat low



(a) (b) (c) (d)

Figure 13.28: Cymat high after melting (15 wt% cryolite) (a) metal phase; (b) salt flux; and Cymat low after melting (15 wt% cryolite); (c) metal phase; (d) salt flux

Table 13.17: Metal yield from the different materials (with 15 wt.% cryolite addition). Note yield refers to the metal recovered relative to scrap, while recovery refers to the percentage of metal that is recovered from the recoverable metal in the material. Also the 99.9 and 100% are achieved since salt is encapsulated by aluminium.

Material	Temperature ^oC	Av. yield (%)	Av.recovery (%)
HYBRIDS			
Hylite 1.2	900	57.6	0.98
Hylite 2.0	900	41.8	0.97
Glare	900	76.0	
Sandwich			
A	800	86.7	94.4
A	900	88.3	96.2
B	800	88.9	97.7
B	900	88.6	97.4
C	800	89.2	97.4
C	900	89.4	97.6
Foams			
Alporas high	900	99.9	
Alporas low	900	100	
Alulight high	900	94.0	
Alulight low	900	95.5	
Cymat high	900	80.2	
Cymat low	900	79.0	

Influence of composition Hylite As can be read from Table 13.17 the metal yield for the Hylite in which the ratio between organics and aluminium is higher than for Glare results in a lower metal yield.

Influence of surface area in Sandwich As can be read from Table 13.17 the metal yield Sandwich A/ and Sandwich B and C decreases considerably due to large oxidized surfaces, as well as the construction of the materials in which the adhesive and surface coating are leading to loss of the metal and prevents metal coalescence. The metal yield for the Sandwich B is lower due to a higher organic content of the material. The effect of a lesser presence of the honeycomb core, which will reduce the decreased metal yield due to the large surface to mass ratio, is so low that this does not become clear from the melting tests. The lower metal yield/recovery of Sandwich A at 800°C is caused by the larger surface to mass ratio of Sandwich A compared to Sandwich B and C. The metal yield/recovery increases when Sandwich A is melted at a temperature of 900°C. At a higher temperature, the viscosity of the salt flux decreases, which will improve the metal coalescence. The melting results for Sandwich A and Sandwich B and C under a salt flux without addition of cryolite are not given in Table 13.17. No metal is recovered for both materials.

Al yield for foams

Influence foaming gas All three foam types investigated are foamed with an inert foaming gas, which prevents the metal pore surface from oxidation during and after production (in case of a closed pore foam). Therefore, no influence of the foaming gas can be concluded based on the material types investigated and the foaming gasses used. The Ti used in a foaming agent (TiH_2) is found in the metal after melting, implying the release if H_2 during melting, which has negative consequences for the metal structure after melting.

Influence density For each of the foam types a high and low-density application is molten to investigate the influence of density on the metal yield. Many properties of the foams are related to the density. The specific pore surface of the foam is related to the density, which is of influence on the metal yield only if the pore surface was oxidised during production or use. From the melting results, no significant difference can be observed between the high and low-density foams. Due to the use of inert foaming gas for production of the foam, the pore surface is not excessively oxidised to irrecoverable alumina. The influence of density on the metal yield will only become visible if e.g. air is used as foaming gas, leading to oxidisation of the surface.

Influence additives/stabilisers The influence of the additives/stabilisers becomes clear from the melting results for the different foam types. The yield of the Alporas foam is difficult to measure because of enclosed salt flux in the metal beads, but is lower than 100%. The added stabilisers are of minor influence on the metal yield, but can be of significant influence on the quality of the recycled metal and on its potential use. The Alulight foam is produced from an aluminium powder and therefore contains a high ratio of alumina, due to the oxidation of the large surface of the powder. TiH_2 is added as foaming agent and will be present in the metal phase. The Al_2O_3 is irrecoverable from the scrap and will lead to a decreased metal yield. The salt flux is more contaminated than for the Alporas foam. These contaminants are losses for the melting operation. The Cymat foam contains 10-20% SiC as a stabiliser for the foam, and in some cases (depending on production route) alumina which is irrecoverable from the scrap. As discussed it is known from previous studies that the presence of organics in the scrap will lead to losses during the melting operation. A thin black layer covers the metal phase of the Cymat foam; this is the possibly pyrolysed organic material (SiC). The salt flux is darker and more contaminated than for the other foam types. The final metal yield is significantly lower due to the presence of stabilisers in the foam.

New aluminium applications in passenger vehicles

The melting experiments as performed for the new aluminium based materials show a decrease in metal yield dependent on specific characteristics of the materials. When applying these types of materials in passenger vehicles, it is clear that the total recovery (recycling) rate of the car will decrease when compared to the use of normal aluminium components. The total decrease in the recycling rate of the car is obviously dependent on the amount of these materials present in the car in relation to the other materials. To exactly determine the influence of the use of aluminium foams on the recycling rate of the car, the composition of the car must be well known. The recoveries for all different materials in the car, including the new aluminium applications, over various recycling processes (mechanical separation and metallurgy) must be known or calculated in order to determine the total recycling rate of the car. However, the application of these new aluminium based materials can reduce the vehicle weight and thus the fuel consumption of the car, leading to a better balance between the reductions of environmental impact due to decreased vehicle weight and increased material losses and emissions. This would require a Life Cycle Analysis study, which also includes the environmental consequences of material losses as well as the negative effect of the creation of untreatable residues during melting of these new aluminium applications.

13.2.8 Treatment of liquid metal

The charge of a cycle is calculated to produce metal of a chemical composition that has been ordered by a customer. The calculation of the charge is based on representative scrap samples, i.e. it is assumed that the melting result of such a sample is applicable to the whole scrap lot. That in fact is only statistically correct. Between the result of a sample and the actual composition of the whole scrap lot there is a statistical variance. Consequently the composition of the molten metal approaches the ordered composition, but usually needs slight corrections with respect to individual chemical elements. Therefore molten metal is tapped through a system of launders into holding furnaces, in which the chemical composition is corrected and some limited refining steps are carried out. The metallurgical work to be carried out in these holding furnaces takes time, therefore the holding capacity of such furnaces is laid out at about 220% of that of a melting furnace, i.e. 2 rotary furnaces are connected to a holding furnace. For example rotary furnaces of 20 t holding capacity each may produce on average 14 t of molten metal/batch and the respective holding furnaces shall hold about 30 t of liquid metal.

Alloying

Remelters in principle produce metal of the same composition of the scrap delivered to them. In some cases the customer may request that the remelters adjust the metal composition with regard to minor elements. Refiners, however, produce cast alloys of standardized compositions irrespective of the scrap alloy compositions. Customarily two main elements have to be added to the metal tapped from rotary furnaces: Si and Mg. The scrap menu of a refiner plant consists of cast and wrought alloys; the latter is needed to dilute exceeding contents of troubling elements. This dilution causes a notoriously low level of Si-content, therefore Si is needed for almost every melt. The average content of Mg in scrap is also suppressed by the dilution effect, but is decreased by the much higher burn-off rate during melting. Thermodynamic calculations support the theory, that little NaCl reacts with magnesium metal in the alloy to form $MgCl_2$ and sodium metal, which is quickly oxidized (typical yellow flames on the surface of molten salt flux); the formed Na_2O reacts with $MgCl_2$ to form NaCl and MgO. The extraordinary high MgO-content of NMC separated during salt flux processing is the result of such indirect Mg-oxidation. Cast alloys with higher Mg-contents therefore require addition of Mg (usually as Mg-scrap) to compensate the over-proportional loss of Mg. Alloying or holding furnaces are customarily tiltable box-type hearth furnaces. Once the melting furnace is ready for tapping a metal sample is taken (or during tapping directly from the metal flowing through the launders). Depending on possible deficits of alloying elements, pure metals such as Si, Cu, Zn, Mn, Ni or Mg are added. These metals are added according to their densities and melting temperatures. For fast dissolution the melt has to be agitated, usually by a gas lance using nitrogen or argon gas. Further metal samples are taken to control the accomplished composition. If the content of an element exceeds the target the melt has to be diluted by pure aluminium metal. After alloying grain refinement is carried out following three different approaches (details are described in the respective literature on secondary aluminium melting techniques):

- fining grains of primary aluminium alloy structure (=fining of grain),
- fining the aluminium-silicon eutectic (= refinement), and
- fining the primary silicon segregation (= silicon fining).

De-gassing

Oxides as well as hydrogen are introduced into the molten metal through the alloying elements. Hydrogen is the only gas that is significantly soluble in aluminium metal as defined by the following equations [360]:

$$log[H]_{Al} = \frac{1}{2} \times \log P_H - \frac{3042}{T} + 0.459 \ (400 - 660°C) \tag{13.42}$$

$$log[H]_{Al} = \frac{1}{2} \times \log P_H - \frac{3086}{T} + 1.467 \ (660 - 1050°C) \tag{13.43}$$

where

$[H]_{Al}$ = concentration of hydrogen in metal ($cm^3/100$ g Al)
P_H = partial pressure of hydrogen (hPa)
T = temperature of metal (°C)

The hydrogen solubility is influenced by alloying element added:

- Mg and Ti increase the solubility, and
- Cu, Mn, Ni, Si, Zn and Sn decrease the solubility.

Unfortunately even the moisture content in the ambient air is a source of hydrogen for liquid aluminium alloys i.e. water vapour is decomposed by liquid aluminium and the generated atomic hydrogen is immediately dissolved as defined by Eq. 13.44.

$$2\mathrm{Al} + 3\mathrm{H_2O} \rightarrow \mathrm{Al_2O_3} + 6[\mathrm{H}]_{\mathrm{Al}} \tag{13.44}$$

The simultaneously generated oxygen causes stoichiometric aluminium oxide formation that floats to the surface of the metal bath i.e. moisture also adds to dross formation. The partial pressure of moisture in air is about 1-2 hPa , which in extreme cases could go up to 6 hPa. The partial pressure of water vapour in the flue-gas from oil or gas burners is much higher and corresponds to 125 and 195 hPa respectively. The water vapour in the flue-gas is responsible for the notorious hydrogen contents in molten aluminium alloys of 1-2 $cm^3/100g$. Porosity of aluminium alloy castings is mainly caused by dissolved hydrogen. High quality alloys require a hydrogen content of < 0.1 $cm^3/100g$, therefore molten aluminium alloys have to be de-gassed prior to casting. This can be accomplished by vacuum de-gassing or purging gas treatment. To this day vacuum treatment has not been successful in secondary aluminium smelting. Purging gas treatment is carried out with inert gasses like argon or nitrogen. Both of these gasses have almost no effect on removal of troubling elements. Gasses containing chemically reactive components like chlorine gas (up to 15 vol.% Cl_2) are also effective in removing hydrogen, but also remove alkali- and earth-alkali-elements in the sequence $Sr > Na > Ca > Li > Mg$ by forming their respective chlorides. These chlorides adhere to the generated gas bubbles and are transported to the bath surface. By this desirable flotation effect other solid impurities, e.g. oxides, are carried to the surface and removed as dross. The effectiveness of the purging gas treatment (including its flotation effect) is influenced by the average size of the gas bubbles (1 liter of gas dispersed into bubbles of 1 mm diameter offers a surface of 6 m^2) and by the quality of the purging gasses. Numerous methods are used to generate small sizes of gas bubbles to achieve an effective removal of hydrogen, wowever, even traces of water vapour in the purging gasses will ruin the purging treatment.

Other refining methods

Molten aluminium alloys could be contaminated by constituents dissolved in the metal or by solid particles dispersed therein. One of the most detrimental dissolved constituents is hydrogen; fortunately hydrogen is effectively removed by purging gas treatment. Other dissolved constituents are elements, which could be alloying or troubling elements such as Li, Na, Ca, Sb, Pb, Fe, Mg, Bi, Sn or Zn. As already mentioned the alkali- and earth-alkali metals can be removed by using purging gasses which contain chlorine gas. For the other elements there is no economically feasible refining method applied in the melting practice. Liquation of heavy metals (Fe, Mn, Si, Cr) occurs when melting highly alloyed scrap. Secondary aluminium smelters use an empirical liquation factor (Fl), which is a function of the composition of the melt and its temperature:

$$Fl = wt.\%\mathrm{Fe} + 2 \times wt.\%\mathrm{Mn} + 3 \times wt.\%\mathrm{Cr} \qquad (13.45)$$

The factor 2 and 3 express that in the liquation residue the contents of Mn and Cr are 2- and 3-times higher than in the original melt. Below $Fl = 1$ no liquation for the eutectic composition is accomplished. The liquation factor is in fact rather used to determine the overheating temperature necessary to avoid unwanted liquation than to carry out a kind of refining; the time necessary to achieve considerable refining results would be unacceptably long. The increasing complexity of scrap composition (Li-removal from AlLi-alloys used in air craft industry) and the quality of produced alloys will certainly promote further refining methods that are not yet economic. At the moment careful alloying with pure elements and accurate control is one of the essential preconditions for the production of standardized alloys out of poorly defined scrap. Dispersed solids in the molten metal could stem from the scrap charge, carried in by alloying elements or generated by water vapour. All particles that are removed end up in the dross, which is usually recycled directly in-house to melting furnaces. The salt flux formed when melting this dross is the outlet of the internal material cycle of secondary aluminium smelters too. Any troubling particles not absorbed by the salt flux will eventually show up in the holding furnaces again. Finally the surface of the metal bath is cleaned by skimming the layer of products of the oxidation and other reactions. The hot skim dropped into a box or ladle is from then on called dross. Due to capillarity effects the solid particles, when skimmed, carry forward up to 80 wt.% entrapped liquid metal [371]; the average hot dross contains about 60 to 70% liquid metal. After dross skimming the melt is left for about 0.5 to 1 (in max. 2) hours to settle. Very fine particles tend to remain dispersed in the liquid metal. For this reason filtration of liquid metal shortly before casting has become common practice. Even though this filtration is very complex, the filters used are very effective, e.g. net-like fibres of glass or refractory material, piles of loose alumina or coke particles, ceramic foam filters or rigid media filters. It is good practice to return the spent filters to the rotary furnaces, where all refractory, oxide or ceramic particles are carried over to the salt flux thereby leave the aluminium recycling system. After the various treatments described above the metal is conveyed through heated launders to the casting machine.

Casting

Wrought alloys, produced by remelters, are customarily cast by continuous casting into slabs or billets for rolling and extrusion respectively. Considering the internal recycling of dross the plant yield of remelters, i.e. t slabs or billets/t of clean scrap input, is between 94 and 97%. Molten cast alloys are usually poured into ingot moulds of different size and shape, e.g. as ingots on casting machines or as slabs by horizontal continuous casting. For better handling foundries prefer staples of 500 to maximum 1000 kg. The most common ingot or slab size is 5 to 8 kg each. An ingot-casting machine should be able to pour within max. 2 hours the complete content of a holding/casting furnace to avoid the risk of liquation of heavy metals. A 30 t holding furnace would consequently need a casting machine with a speed of pouring of >15 t/h.

Liquid metal transportation

Decades ago some continental European secondary aluminium smelters supplied near-by large foundries with liquid aluminium. In the meantime some secondary aluminium smelters produce more than 80% as liquid metal. The large foundries of the big continental European automobile manufacturers are now prevailingly supplied by liquid aluminium alloys, advantages being obvious:

- metal arrives at the consumer "just-in-time" ,
- consumer does not need a melting furnace,
- liquid metal supply saves energy and emissions,
- "just-in time" delivery saves storage facilities, and
- recycling cost are significantly reduced by liquid metal supply.

The hot metal is tapped into preheated transportation ladles with a temperature of well above 800°C. The empty ladles weigh about 4.5 t and have a holding capacity of 4.5 t liquid metal. Special trailers can load 3 to 4 of these ladles, i.e. per truck haulage 13 to 18 t of liquid metal can be delivered. The complete transportation system is in the meanwhile certified. In Germany approximately 50% of the total refiner output is transported as liquid metal. The ladles are well insulated and the drop of temperature is approximately 10 - 20 °C/h, i.e. the metal can be kept liquid for about 8-10 hours, depending upon the overheating temperature. Consequently the maximum trucking distance is about 4-5 hours for one way, as in case the customer is unable to accept the metal it has to be brought back to the smelter still in the liquid state. The technical performance of this liquid metal transportation has achieved a high grade of organisation (even in continental winter seasons), the foundry-plants of the big automobile manufacturers have therefore become almost completely dependent upon this kind of metal supply.

Example 13.7
A secondary aluminium smelter casts ingots at a casting temperature of 770° C. The theoretical heat requirement to bring cast alloy metal to this temperature is 1265 MJ/t of metal. At the cast-house of the customer 15 t of ingots are delivered, re-melted and the metal is cast again at 770° C. The heat requirement is an additional 1265 MJ/t of metal. The total heat invested is theoretically 2 × 1265 = 2530 MJ/t of casting. Now the smelter delivers the 15 t as liquid metal, however, overheated up to 830° C. The theoretical heat requirement is 1475 MJ/t of metal. The preheating of the transportation ladles needs about 30 m^3 gas/t liquid metal or 1050 MJ/t metal. After 3 hours driving time the metal arrives at the customer's foundry with a temperature of 770° C and is immediately cast. Considering an overall heat efficiency of the melting furnaces of 33%, the supply of the 15 t of liquid metal saved approximately (2530/0.33/35 - (1475/0.33/35 + 30)) × 15 = 920 m^3 natural gas (net combustion heat of natural gas 35 MJ/m^3).

It should be noted that a truck transporting 15 t of liquid metal (and 15 t of ladles) could easily carry 30 t of ingots. Net transportation costs of liquid metal are therefore sizeably higher than for ingots.

13.2.9 Emissions

The composition and the contaminations of old aluminium scrap reflect the kind of usage of the respective products.

Gaseous emissions

Organic contaminations typically adhering to collected old scrap, like cutting oils on swarf, paints or plastic on sheet and foil, will be partly burned and partly cracked in plants for drying oily chips and swarf, de-coating of UBC, pyrolytic treatment of packaging material, or by direct melting of collected scrap. The resulting gaseous emissions are components like CO/CO_2, H_2O, and gaseous HCl, HF and Cl_2 (from purging with chlorine containing gasses), depending upon the type of organic substance. The melting temperature, the oxygen partial pressure in flue-gas and the unavoidable presence of metal oxides promote the formation of PCCD. Modern gas-cleaning installations and the injection of lime and absorbent additives (in the order of magnitude of in total 1 g/m^3 off-gas) into the off-gas stream meet limit values for gas emissions. e.g. <20 mg $dust/m^3$, < 0.1 ng TE/m^3.

Aqueous emissions

There are no aqueous emissions from the secondary aluminium melting.

Solid emissions

The solid emissions comprise salt flux, bag house filter dust, dross and spent refractory lining from furnaces. The salt flux generated by refiners is listed as hazardous waste and in Europe it is completely processed. The metal and salt content of this flux is returned to the refiners. The NMC residue is prevailingly used in the cement, cobble stone and mineral fibre industry. Smaller fractions may be used for stabilization of landfills or similar underground construction. As a rule 0.5 t of salt flux is generated per t of refiner production. From this 0.5 t of flux about 180 kg of dry NMC residue is produced, which represents the total amount of accumulated NMC of the whole aluminium usage cycle. In the order of magnitude of 10 to 25 kg of bag house filter dust are generated in refiner smelters, this includes the lime and additive addition, if not recycled back to the melting furnaces. Approximately 50 -75 wt.% of the dust is water-soluble, consisting of evaporated KCl and NaCl, $CaCl_2$, CaF_2 and $CaSO_4$ stemming from the reaction between hot off-gas and injected lime. The remaining components are oxides of aluminium and its alloying elements, carbon and organic substances - among it PCCD and PCCF (between 5 and 40 μg TE/kg of dust). The dust is listed as hazardous waste, the disposal cost are correspondingly high. As a consequence of the extremely low bulk density of only 0.2 - 0.25 t/m^3 (or 0.4 - 0.45 t/m^3 jolt squeezed) the transportation cost are also high. Therefore several attempts have been made to process this residue. Only one commercial scale plant has ever been in operation (operated by Ur-Chemie in Germany) but has been closed since 2000. This dust processing plant had a through-put capacity of 10 000 t dust/a, sufficient to process the bag house dust of all the German refiners. The fate of this plant is a typical consequence of the economics of scale. The rather complicated thermal and chemical process was based on a very limited and small tonnage. Therefore even with full capacity the break-even cost were 250 €/t dust, i.e. very high. The re-unification of Germany instantly made available a huge volume of excavated underground salt mines in East Germany, which could be used as underground disposal facilities. The prices for this kind of disposal fell and were sustainably lower than the break-even cost of the dust processing plant, resulting in the closure of the dust processing plant as mentioned above. The refractory lining of the different furnaces are replaced because of continuous wearing. The fluoride additives in particular chemically attack the refractory lining which leads to a systematic abrasion and erosion of the refractory bricks. In rotary furnaces the inner lining consists, for example, of refractory bricks with a thickness of 250 mm. Two years results in about 200mm of wear and the complete refractory lining has to be replaced. A rotary furnace of 2.75 m inside diameter and 5 m inside length loses about 1.4 kg brick lining/t melted metal in 2 years. The remaining brick work, replaced every 2 years, adds up to about 0.4 kg/t metal; in literature the generation of 2 - 3 kg worn brick work/t metal is mentioned [360, 382], i.e. the difference consists of products of chemical reactions and penetrated material like metal and salt flux. No practical process to treat the small tonnage of spent refractory brick work exists. This waste is therefore completely land filled (in Europe about 5000 t/year or (t/a)). Dross from the flux-free melting and from the holding furnaces is usually processed and subsequently returned to refiners, where it is melted under flux. Dross is not a residue of aluminium recycling but an intermediate and valuable carrier of the accumulated NMC that finally ends up in the salt flux.

13.2.10 Products

Prompt clean scrap, usually of one particular wrought (very rarely cast) alloy from extrusion plants or rolling mills, is delivered to secondary aluminium smelters for re-melting only i.e. a remelters. The product of such re-melting is a slab or billet of the original chemical composition. Old collected scrap, customarily contaminated by various foreign metals (those metals that are either not used in alloying, or are minor alloying elements of aluminium) is usually processed prior to melting. Statistically a significant part of such foreign metals cannot be liberated and separated during scrap processing and remain with the scrap. The content of alloying elements (preponderantly Si, Fe, Cu) in scrap is far too high to be converted into wrought alloys, with their low level of alloying elements. These refiners have to deal with the adjustment of chemical compositions of alloys by use of (in fact limited) refining methods, their product are cast aluminium alloys.

Standard alloys

Several European countries have developed their own standards for aluminium alloys. In the meantime EU standards (EN A: EN AC castings, EN AW wrought alloys, EN AM master alloys) are available and have replaced national standards. However, in order to compare previous publications the old national standards have to be known. The following list of publications on standards [359] can be used for comparison.

- Key to Aluminium Alloys, Aluminium Verlag, Düsseldorf
- Handbook of International Alloy Compositions and designations, Vol. III, Aluminum.
- Registration Record of International Alloy Designations and Chemical Composition Limits for Wrought Aluminum and Wrought Aluminum Alloys, published by Aluminum Association (AA), Washington, USA.

- Metals Handbook, American Society for Metals, Metals Park, Ohio, USA

Various aluminium-focussed journals such as ALUMINIUM publish the most recent status of standardization in the EU. The list of standardized cast aluminium alloys is confusingly long. In spite of this the number of cast alloys ordered by the customers and produced by the refiners is very small, the main cast alloys produced in Europe summarized in the following:

EN AC 46000, 46200, 46500	AlSi9Cu3, AlSi8Cu3, AlSi9Cu3(Fe)(Zn)
EN AC 43000, 43100, 43400	AlSi10Mg, AlSi10Mg(Fe)
EN AC 44100, 44200, 44300	AlSi12, AlSi12Fe
EN AC 47000, 47100	AlSi12Cu, AlSi12Cu1Fe

This small number of standardized cast alloys shows that the majority of the production of refiners is cast alloys with silicon contents of between 9 and 12%. Collected old scrap is a mixture of cast and wrought scrap e.g. from shredding contemporary high aluminium containing automobiles (e.g. Audi A8). There is no large-scale technology available yet to sort wrought from cast aluminium alloys. Consequently the level of silicon content in all scrap delivered to refiners is well above 5%, which makes it impossible to produce wrought alloys with a Si-content of <1%. A dilution of such scrap feed to produce wrought alloys is also impossible.

Example 13.8

A refiner produces an alloy with 5% Si that should be diluted by primary metal to a content of 1% Si. There is primary metal available with 0.2% Si. The necessary amount of primary metal is 6 t primary metal/t of 5% Si containing alloy. The economic situation would be as follows: Melting cost are 250 €/t produced metal, contracted sales price for 1% Si alloy is 1500 €/t, primary metal cost 1450 and scrap 1200 €/t produced metal. Actual cost of produced metal is $(1200 \times 1 + 5 \times 1450 + 6 \times 250)/6 = 1660$ *€/t produced metal. The loss of the refiner would be* $1660 - 1500 = 160$ *€/t produced metal.*

Master alloys

Master alloys are added to molten alloys for adjustment of the chemical composition or the texture. Master alloys are standardized as well and have an accordingly precise composition; therefore the production of such master alloys from scrap is rather limited. On the other hand scrap lots are often delivered with such heterogeneous composition and/or contamination that representative sampling is in fact impossible. In such cases the whole lot is melted without adding any elements to a so-called recycled secondary ingot (RSI), which is then analysed and registered. RSI are categorised in high, medium and low Cu-containing material and traded as a special kind of "master-alloy" for further cast alloy production.

Forms and sizes

Wrought alloys are produced in form of slabs for rolling and billets for extrusion. Slab formats are 300-800 mm thick, 900-2500 mm wide and 4-8 m long, depending upon the capacity of the holding furnaces and continuous casting equipment of remelters. Likewise the size of billets is dependent upon the installed equipment: 120-800 mm diameter and up to 8 m long. The endless lines are then sawn into the appropriate length. Cast aluminium alloys are usually cast into ingots of an individual weight of 4 - 10 kg. The ingots are stapled on pallets cast from the same alloy. The total weight of a staple is stipulated by the receiving foundry and customarily 500-1000 kg. As the strips used for sizing are made of aluminium as well the complete staple can be charged into the casting furnaces at the foundry. Sows or jumbos are huge ingots of 400-500 kg each. Such ingots are used for remelting or more typically for RSI (recycled secondary ingots). Special formats for aluminium are granules (3-20 mm), shot metal (0.4-3 mm) and aluminium powder (<0.4 mm). Although representing only a small fraction of the wrought and cast alloys production these products have a crucial function in certain application areas, e.g. for steel de-oxidation, metal blasting, aluminothermic metal winning, powder metallurgy, metal foams and pigment fabrication. The consumption of de-ox aluminium is about 2 kg/t crude steel, i.e. in Europe approx. 250-300 000 t de-ox aluminium granules may be consumed. The quality shall be >97% Al(+Mg), and <0.5% Cu and Zn each. Due to these constraints secondary aluminium smelters are only able to produce de-ox aluminium from unalloyed scrap, which is rare and the production relatively small. Nevertheless, almost 50% of the German de-ox consumption is produced by secondary aluminium smelters. The production of finer material is not more than several thousand tons/a all over Europe, and only a fraction of this already small tonnage is produced from recycled aluminium metal.

Chapter 14

Simulating a rotary furnace for aluminium recycling

The preferred melting furnace of European refiners is still the rotary furnace. Typically refiners can only analyse the melting operation retrospectively and therefore have only feedback control i.e. they can only learn from the past. Competitions for limited scrap volume and ongoing cost pressures force refiners to use feed-forward control for their operation, implying that a smelter can predict the melting yield of any type of scrap.

Therefore, the objectives of the simulation of the rotary furnace is to increase metal recovery, decrease operating costs by decreasing the cycle time *(a good average might be 4.75 hours/cycle, a cycle meaning the time from metal tap to metal tap)* and providing feed-forward control capabilities.

These aspects are the principle theme of this chapter, which summarizes research work together with Karl Konzelmann Metallschmelzwerke (KKM) in Germany the authors developed new feed forward control models which include (i) a combined mass and energy balance based on well control sampling and applying all the data that was generated as discussed in Section 13.2, and (ii) a fundamental fluid flow model based on computational fluid dynamics.

14.1 Mass and energy balance model

This section discusses the development of an integrated mass and energy balance model, that permits the smelter to reliably predict the melting yield of different categories of scrap as a function of the numerous parameters that have a noticeable effect on the furnace performance as depicted by Figure 14.1.

From an analysis of the various influential parameters, it became evident that one obviously very important parameter is in practical terms inaccessible to measurement i.e. the burn-off rate of metal inside the rotary furnace. Figure 14.2 briefly depicts the importance of the burn-off rate i.e. it is influenced by and has influence on many other parameters. Two aspects immediately became evident from this analysis:

- a rotary furnace for melting contaminated scrap is an extremely complex system i.e. the system behaviour is almost unpredictable, and
- the burn-off rate of metal is crucial to the technical and economic performance of a rotary furnace.

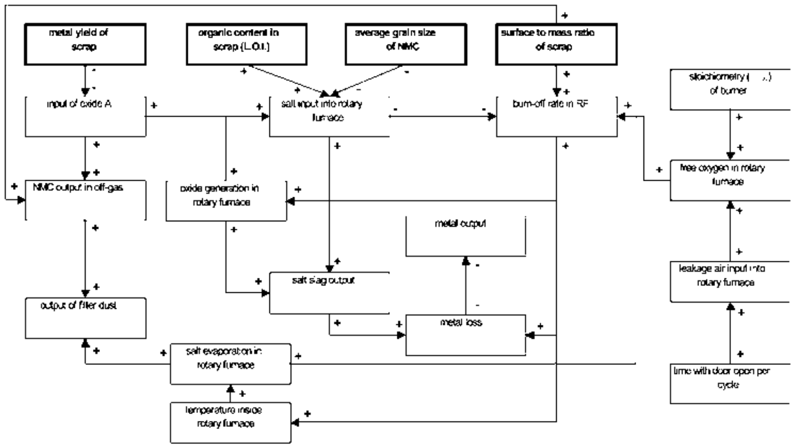


Figure 11.1: Influence of crucial properties of scrap on typical furnace performance criteria. The (+) sign indicates that an increase of the preceding parameter causes an increase of the following parameter or criterion. The (-) sign indicates an opposite behaviour. For example: (+) means, if the oxide generation in the rotary furnace increases the salt flux output will rise as well; (-) means, if the particle size of NMC decreases the salt input into the rotary furnace has to be increased.

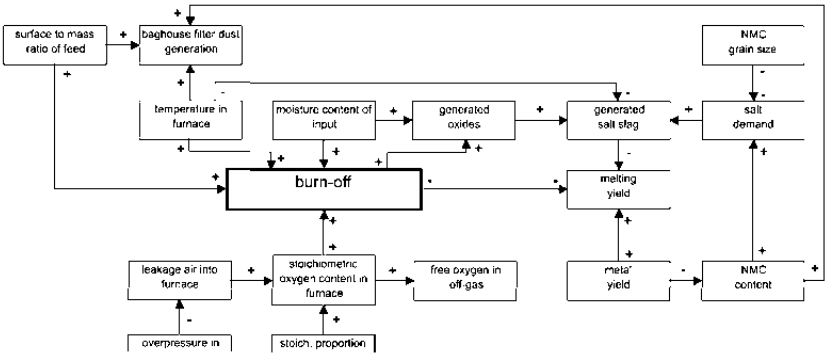


Figure 14.2: Influence of burn-off rate on typical furnace performance criteria

In this context burn-off rate is defined as the percentage of the metal content in scrap, which is converted to oxide inside the furnace. A source for oxygen is e.g. air sucked into the furnace through leaks or through the opened door or water vapour and carbon dioxide that are products of natural gas burning for heating the furnace. Oxidation reactions are exothermic and may occur according to the following equations:

$$2\mathrm{Al} + \frac{3}{2}\mathrm{O}_2 \rightarrow \mathrm{Al}_2\mathrm{O}_3 \tag{14.1}$$

$$8\mathrm{Al} + 3\mathrm{CO}_2 \rightarrow 2\mathrm{Al}_2\mathrm{O}_3 + \mathrm{Al}_4\mathrm{C}_3 \tag{14.2}$$

$$2\mathrm{Al} + 3\mathrm{H}_2\mathrm{O} \rightarrow \mathrm{Al}_2\mathrm{O}_3 - 3\mathrm{H}_2 \tag{14.3}$$

14.1.1 Mass balance model for the rotary furnace

Since most of the boxes in Figure 14.1 also represent a mass distribution function (split factor), a comprehensive and detailed mass balance for a rotary furnace was set up. A subsequent detailed energy balance was based on the results of the mass balance. Various unknown parameters such as dust carry over, salt evaporation, entrapped metal in flux, burn-off as a function of scrap type etc. have been fitted to the model and continuously checked for plausibility.

The rotary furnace selected for the modelling is a 20t rotary furnace at Konzelmann's refining plant at Hannover (Germany), fired by natural gas and oxygen burner situated on the charge-end side. The inside of the rotary furnace was equipped with paddles of cast iron mounted directly on the outside steel shell. The structure of the mass balance is represented by Table 14.1, derived subject to the following assumptions:

- at temperatures of around 800°C aluminium oxide cannot be reduced to metal by carbon or hydrogen, therefore the oxide content of scrap (e.g. adhering to the surface as a result of corrosion) will remain oxide,
- the metal content of the scrap must be found as metal or as oxide if burnt inside the furnace,
- there are two main outlets for metal i.e. tapped liquid metal and entrapped metal in salt flux.
- NMC whether adhering to the scrap or generated during melting report to the salt flux and bag house filter dust, therefore accounts for all non-metallic and non-volatile constituents in any of the mass flows, and
- the model is based on the predominantly produced standardized alloy AlSi9Cu3 (EN AC 46200) *(composition in Table 14.2)* as basis with all the main alloying elements Al, Si, Cu, Fe, Zn, Mn, and Mg included,

In order to calibrate the model the listed parameters were varied until the mass balances for all alloying elements were closed. It is worthwhile to mention the content of some aluminium compounds others than $\mathrm{Al}_2\mathrm{O}_3$ or spinels are listed Table 14.3.

Some derived parameters from the mass balance model of the furnace:

Total furnace capacity	20 t
Average metal yield of scrap feed	92.3 %
Salt factor used by operators	1.5

Table 14.1: Structure of the mass balance summarised as input and output

	Total (sub streams)	Metal	NMC 1	NMC 2	Salt	Moisture
Scrap	scrap_{total}	scrap_{metal}	0.00	scrap_{NMC2}	0.00	$\text{scrap}_{moisture}$
Salt	salt_{total}	0.00	0.00	0.00	salt_{salt}	$\text{salt}_{moisture}$
Total	total_{in}	$\text{total}_{metal\ in}$	0.00	$\text{total}_{NMC\ in}$	$\text{total}_{salt\ in}$	$\text{total}_{moisture\ in}$
Metal	metal_{total}	metal_{metal}	0.00	0.00	0.00	0.00
Salt flux	salt_{total}	salt_{metal}	salt_{NMC1}	salt_{NMC2}	salt_{salt}	0.00
Offgas (gas+dust)	offgas_{total}	0.00	0.00	offgas_{NMC2}	offgas_{salt}	$\text{offgas}_{moisture}$
Total (main streams)	total_{out}	$\text{total}_{metal\ out}$	$\text{total}_{NMC1\ out}$	$\text{total}_{NMC2\ out}$	$\text{total}_{salt\ out}$	$\text{total}_{moisture\ out}$

Table 14.2: Used composition of alloy AlSi9Cu3

Element	wt.%
Si	9.5
Cu	3.0
Mg	0.3
Zn	1.2
Fe	1.3
Mn	0.55
Ni	0.55
Ti	0.25
Cr	0.15
Al	82.35
Others	0.85

Melting recovery of sampling station	98.5 %
Moisture content of scrap	1.0 wt.%
Moisture content of salt flux	2.0 wt.%
Entrapped metal in salt flux	8.0 wt.%
NMC carry-over	5.0 wt.%
Salt evaporation	2.0 wt.%
Metal burn-off rate	2.5 wt.%

Table 14.3: Content of some aluminium compounds

Compound	average content in flux
Al_4C_3	1.6 wt.%
AlN	0.52 wt.%
AlP	0.028 wt.%

14.1.2 Energy balance for the rotary furnace

The energy input comprised of (i) the heat value of natural gas/oxygen and heat of combustion, and the heat of reaction of metal oxidation. Other assumptions for the energy balance include:

- composition of the natural gas 87.1 vol.% CH_4; 1.2 vol.% C_2H_6; 0.1 vol.% C_3H; 0.1 vol.% C_4H_{10}; 0.8 vol.% CO_2 and 10.7 vol.% N_2
- for a burner setting of $\lambda = 1.05$ the net heat value was 32.45 MJ/m^3 natural gas (STP),
- flame temperature of the gas-oxygen burner is 2900°C considering the dissociation of CO_2 and H_2O,
- on the basis of thermochemical data the heat of reaction for the oxidation of all the alloying elements Al, Si, Mg, Cu, Zn, Fe, Mn, Ni, Cr, Ti as well as the heat of formation of AlN, AlP and Al_4C_3 at all temperature have been modelled and included,

- old scrap contains various fractions of plastic material, assumed of pure aliphatic character i.e. of the structural formula C_nH_{2n+2}, however for the sake of calculability was simplified to CH_2,
- according to the content of aluminium-carbide in a salt flux processing plant a "carbidisation" factor has been introduced to mathematically describe the formation of carbide by partly burned or cracked organic substances in the scrap according to:

$$4Al + 3CH_2 \rightarrow Al_4C_3 + 3H_2 \tag{14.4}$$

$$2CH_2 + 3O_2 \rightarrow 2CO_2 + 2H_2O \tag{14.5}$$

$$6H_2 + 3O_2 \rightarrow 6H_2O \tag{14.6}$$

- net heat of reaction of all the reactions was calculated to be 31.34 MJ/kg of oxidised Al-alloy,
- various calculated data are summarized in Table 14.4, and
- heat losses calculated by a computational fluid dynamic model are summarized in Table 14.5 (see Appendix A.3).

Table 14.4: The latent heat of various streams used in the model

Material	Latent heat
Heat in tapped metal (770°C)	1265 MJ/t tapped metal
Heat in tapped salt flux (780°C)	1026 MJ/ tapped flux
Heat of dissolution for Si, Cu, etc.	-40 MJ/t metal
Heat in off-gas dust carry-over (950°C)	910 MJ/t dust
Heat in off-gas (950°C)	5.83 MJ/m^3 gas
Heat in leakage air	1.31 MJ/m^3 air
Heat loss through walls	47 137 W
Cooling losses (over weekend)	24 833 MJ/week

The energy balance was iteratively solved together with the mass balance by adjusting for example (i) the salt factor influenced the composition of the feed, the mass and composition of the salt flux, the mass of the metal tap etc. and consequently the energy output, and (ii) any change of burn-off rate would influence temperatures and/or gas consumption, heat losses, salt evaporation etc. which changes the mass balance.

Table 14.5: Heat losses computed by CFD

Heat loss through	MJ/furnace cycle
Furnace cylinder	555
Front + rear end	203
Paddles	160
Total	918

Note that the installed stirring paddles in the furnace increase the heat loss requiring an additional ca. 4.5m^3 of gas and 9.5m^3 oxygen in addition per furnace cycle are necessary to compensate this heat loss. In order to calibrate this model the data tabulated in Table 14.6 were measured.

Table 14.6: Recorded variables during the industrial measurement campaign

Parameter	Unit
Time	sec., min., h
Temperature off-gas	°C
Gas flow	m^3/h
Oxygen flow	m^3/h
Motor drive	A
Gas and oxygen consumption	m^3/cycle
Door open/closed	1/0
Rotation	rpm
Scrap feed	kg/cycle
Flux feed	kg/cycle
Total charge	kg/cycle
Scrap category	-

14.1.3 Results of combined mass and energy balance calculations

The base case was used to stipulate the value of a number of parameters, for which only order of magnitude measurements are available. Such parameters such as salt evaporation, dust carry-over and the content of entrapped liquid metal in salt flux at the moment of tapping were derived from previous mass balance data based on the basis of a full business year. The gas consumption in m^3/furnace cycle was used as the variable to close the energy balance. The aforementioned parameters were varied until the resulting gas consumption was in agreement with the metering. The following base case scenario (Table 14.7) has been used for the sensitivity analysis, but does not necessarily reflect the actual operating parameters of the furnace.

Important data have been derived from the model is the heat necessary to heat 1 t of AlSi9Cu3 from room temperature to typical 770°C tapping temperature: 1265 MJ/t alloy. The equivalent heat in salt flux of the same temperature is 1026 MJ/t salt flux.

14.1.4 Sensitivity analysis with the model

Various sensitivity analyses with the model made very clear that the extent of metal burn-off inside the rotary furnace dominates the technical and economic result of the melting process! The salt factor (SF) is the second most important influence on the furnace operation. The salt factor influences the furnace operation in a rather complicated way, as it effects the reaction heat, the gas consumption, the energy outputs in salt flux, metal, dust and off-gas as well. An increase of the salt factor from 1.5 to 2 for example, requires on average an additional gas consumption of at least 5 m^3/t of tapped metal (plus ca. 11 m^3 of oxygen). Referring to the base case scenario described by the data in this section, the sensitivity analysis produced the following result:

- a decrease of the metal burn-off rate by a relative 33% to base case (e.g. from 3 to 2%) increases the gas requirement by 10 m^3/t of metal,
- a decrease of the salt factor also by a relative 50% to base case decreases the gas requirement by ca. 6.5 m^3/t of metal, and
- a change of any of the other parameters by 50% relative results in an effect of less than ±1 m^3 gas/t of metal.

Table 14.7: A combined mass and energy balance based on the composition of the alloy AlSi9Cu3

Stream	MJ/furnace cycle	Units/furnace cycle
	Mass balance	
Scrap input		17.167 t
Salt flux		2.833 t
Salt flux		5.869 t
Bag house dust		0.062 t
	Energy balance	
Reaction heat	-6180	
Gas burning heat	-29704	915 m^3
Total input	- 35 885	
Heat in salt flux	5 992	5.87 t
Heat in tapped metal	17 894	14.15 t
Heat of dissolution	-559	
Heat in off-gas dust	36	0.06 t
Heat in off-gas	7 644	2548 m^3
Heat in leakage air	2759	2098 m^3
Heat loss through walls	764	
Heat in moisture	874	
Total output	35 404	

14.1.5 Data reconciliation

Any change of the burn-off rate of metal during melting has a dramatic influence on the mass and energy balance. An increased burn-off converts more valuable metal into NMC with the effect of reduced metal sales and simultaneously increased operating cost. Unfortunately this essential operating parameter is customarily unknown and not accessible to any reliable measurements. Therefore data reconciliation was used to back-calculate the most likely burn-off rates for different furnace cycles (see Eqs. 3.1 to 3.5). The described data reconciliation technique was used with particular focus on obtaining a value for the burn-off rate for different categories of scrap with properties summarized in Table 14.8 are summarized in Table 14.9.

Table 14.8: Main features while processing the three groups of scrap categories

Group	Typical scrap	Dust carry over	Moisture in scrap	Metal yield
1	Flux granules, shredded cast scrap, turnings	7%	1%	80%
2	Shredded cast, packaged wrought scrap	2%	0.4%	90%
3	Dross	10%	0.2%	65%

One might be prone to spontaneously generate a curve "burn-off rate = f(metal yield)", however, the number of data is still too small to justify such a generalized function with sufficient statistical accuracy. Nevertheless they give a very first indication of the order of magnitude of an extremely important parameter for melting different but typical categories of contaminated collected scrap. The calculated figures indicate substantial metal losses by oxidation inside the rotary furnace. The results proved some essential and obvious issues:

Table 14.9: Burn-off rates of three groups of scrap categories

Group	metal yield	burn-off rate
1	80%	2.7%
2	90%	2.15%
3	65%	4.4%

- comprehensive data collection is a fundamental basis for any modelling,
- modelling requires an in depth knowledge of the technology and all parameters that affect the process,
- data reconciliation intelligently applied is key to producing realistic results by estimating unmeasurable important parameters, and
- modelling without ongoing adjustments to actual practice is of no interest to industry.

Furthermore, not commanding technology in this depth manner makes any sensible argumentations about sustainable useless!

14.1.6 Smelter balance

Based upon the mass balance of the rotary furnace similar mass balances were established for other melting furnaces of this refiner plant, including the pertinent holding furnaces. For these mass balances each scrap type of a charge has been individually calculated including its specific salt requirement. All these different mass balances were combined into one smelter model. Due to the batch operation the cycle time of each furnace, including gas and oxygen consumption had to be integrated, which were taken from the companies' own operational data.

The basic structure of a mass balance of a melting and holding furnace unit is depicted by Figure 14.3. Internal recycling of holder dross is implied, this dross might be skimmed as hot dross with up to 80 wt.% of entrapped liquid metal, but if not protected against ambient air after skimming the metal content may go down to 35 wt.%. By various protective cooling methods an average metal content of returned cold dross is about 50-60 wt.%. For the sake of transparency the balance uses a basis of 1000 kg feed. In reality the total amount of scrap and salt should sum up to the holding capacity of the melting furnace e.g. 15 or 20 t.

For the calculation of the mass balance, data were used that are within the scope of melting practice but do not reflect the situation at a distinct refiner plant. The variation of any parameter listed in Table 14.11 will change the mass flow and certainly the plant yield. It should again be mentioned that the yield refers to the ton of scrap feed and the recovery to its metal content. The plant yield and recovery refers to the scrap menu and the alloying elements as well, since both are sources of metal arising from outside the system.

The constraint of >47% salt in the flux (Table 14.11) implies that any salt content below that value would definitely result in a so-called sticky flux. The corresponding salt factor, calculated according to refiner practice would be 1.33. If there are critical scrap types within the menu, e.g. bottle caps or printed foil, the salt content of the flux has to be noticeably higher than 47% (see Section 13.2.4). For a complete smelter balance such mass balances have to refer to the actual tonnage/furnace cycle and consider each scrap category as part of the scrap menu. For each refiner the parameters listed have to be evaluated as plant specific figures.

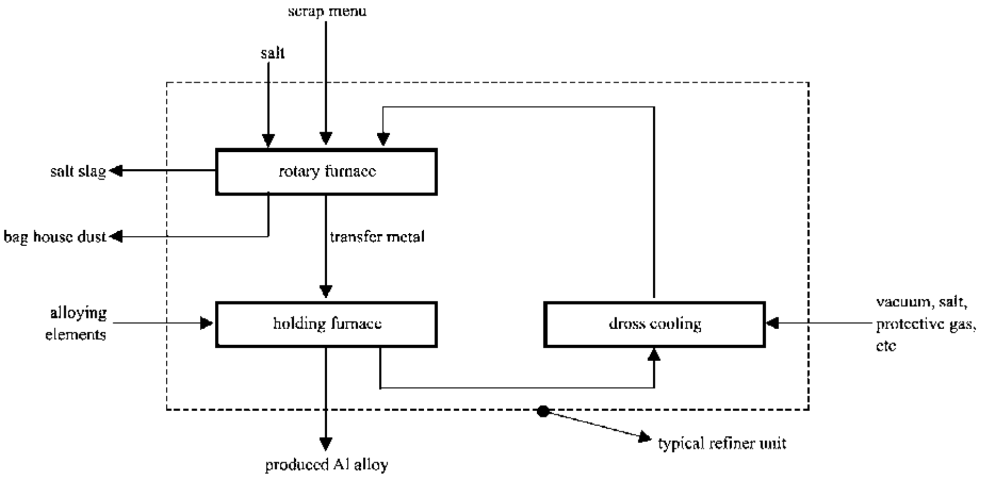


Figure 14.3: The system boundary used for the mass balance model around a typical Al refining plant processing diverse unlcean scrap

Table 14.10: Typical mass balance dataset for a Al refiner plant

Rotary furnace	Total	Metal	Oxide	NMC	Salt
Scrap menu	1000.0	870.0	0.0	130.0	0.0
Cold dross	23.3	12.4	0.0	11.0	0.0
Salt	190.0	0.0	0.0	0.0	190.0
Total charge	1213.3	882.4	0.0	141.0	190.0
Dust	14.0	0.9	0.0	7.0	6.1
Salt flux	391.0	31.3	41.9	133.9	183.9
Transfer metal	828.1	828.1	0.0	0.0	0.0
Holding furnace					
Transfer metal	828.1	828.1	0.0	0.0	0.0
Alloying elements	58.0	55.1	0.0	2.9	0.0
Hot dross	21.5	14.4	4.2	2.9	0.0
Produced metal	866.6	866.6	0.0	0.0	0.0
Dross cooling					
Hot dross	21.5	14.4	4.2	2.9	0.0
Cold dross	23.3	12.4	3.9	7.1	0.0

Table 14.11: Parameters which if varied will change the material flow and plant yield significantly

Metal yield	87 %
Salt content of flux	>47%
NMC carry-over	5%
Salt evaporation	5 kg/t charge
Metal burn-off rate	2.5%
Entrapped metal in salt flux	8%
Alloy element addition	7%
Metal burn-off rate holder	0.25%
Metal content hot dross	67%
Metal content cold dross	53%
Metal burn-off rate in dross	14.1%
Plant yield	81.91 %
Plant recovery	93.68%

14.1.7 Conclusion

This continuous modelling and measuring made the operation at the KKM refiner plant in Hannover transparent and made it possible to answer the question "What happens, if?". Within about 2 years the smelter cost per t of produced metal has been reduced by more than 20%, a combined effect of consumable reduction, and increased scrap throughput and plant yield due to reduced metal loss.

14.2 CFD simulation of a furnace for Al recycling

In a typical secondary aluminium process, the rotary furnace functions simultaneously as a smelter and a phase separator 14.4. It is capable of recycling heavily contaminated scrap [383]. The scrap feed is charged into a rotary furnace, passing through a salt layer, melting, mixing and being cleaned in the furnace. The rotary furnace is normally operated at a temperature around 800°C. Burning of natural gas with oxygen is used as the heat source. The produced liquid aluminium is tapped into a holding furnace, further refined and then directly transported to the industrial partners or cast into ingots. The salt flux with various contaminations should be further processed and reused. The complexity in the process is due not only to the high temperature effect and complex chemical reactions, but also to the highly complex scrap feed with a distributed nature of aluminium types, sizes, shapes, compositions, paintings and other contaminations.

Though the process for reclamation of aluminium scrap has been developed for many years, little public knowledge is available. All data presented in the previous sections of this chapter permits more sophisticated modelling, since a large body of sophisticated data is now available for doing this. Therefore, a computational fluid dynamics (CFD) based process model of scrap melting in a rotary furnace was developed to predicting the melting rate and energy distribution in relation to the scrap types and properties, and to make improvements of the process. Turbulent fluid flow, gas combustion, radiation, and conjugated heat transfer were simulated. To represent the distributed nature of the aluminium scrap feed with different types, sizes, shapes etc., a scrap melting sub-model with population balance modelling (PBM) was developed and integrated into the CFD based process model. The scrap melting sub-model was simplified from the previous developed numerical model for a single aluminium particle

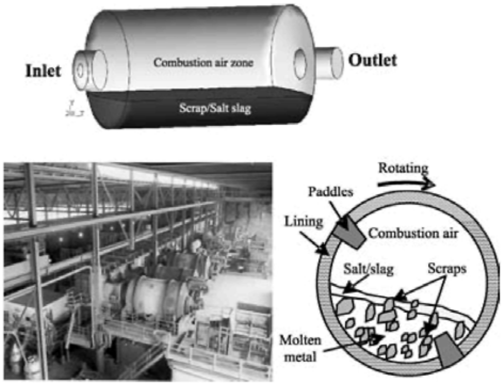


Figure 14.4: Illustration of the rotary melting furnace

melting in molten melts [384]. Furthermore an aluminium burn-off sub-model was developed and integrated to take into account the heat generated due to the burn-off (oxidation) effect during the melting process. Finally a number of case studies were conducted to understand the influence of particle size, shape and quality of the scrap.

14.2.1 CFD framework of the process model

General information of the CFD based process model

Metallurgical processes involve complex phenomena of momentum, heat and mass transport, which play important roles in reaction kinetics and reactor performance. CFD as a research tool was found useful in studying various metallurgical processes. In this study, a commercial CFD package, ANSYS-CFX 5.6®[385], was used as a framework of the process model, coupled with user-developed sub-models. The industrial scale rotary furnace is 3.0 m in inner diameter, 3.65 m in outer diameter including the lining structure and 6.9 m in length. The model consists of a gas region with turbulent flow and combustion as well as radiative heat transfer in the upper part of the furnace, a solid region of the furnace lining, and a solid-liquid region of salt and aluminium metal in the lower part of the furnace. The rotational speed of the furnace is about 1.33 rpm.

Treatment of the scrap-salt zone

The solid-liquid region was regarded as a conducting solid, a mixture of scrap and salt solids. The phase change of scrap melting was handled by the user-developed melting sub-model. Thus the fluid flow in this zone was not considered, while the effect on heat transfer in this zone was represented by a number of thermal parameters. It was assumed that scrap and salt are well mixed. The thermal properties of the mixed material were calculated based on the mass fraction and the phase state of the materials in the mixture. The effective density of this region was calculated based on densities of solid scrap and salt, and it was assumed not to change during the process, despite the effect of thermal expansion. Heat capacity was also defined in a similar way. Some augmentation coefficients for the thermal conductivity of the mixture were applied here to take into account the influence of the voidage in the scrap-salt zone, as well as the effect on heat transfer due to the fluid flow in the scrap-salt zone, agitated by furnace rotation.

Initial and boundary conditions

The initial temperature in the gas zone and the scrap-salt zone was set as 303 K. An initial size distribution of the scrap and salt particles was defined. The initial temperature in the lining structure was imported from a previous steady simulation of heating the empty furnace. The inlets of the burner for natural gas and oxygen are really small compared to the furnace body. In this case the inlet was simplified to reduce the computing time. The profiles of velocity, temperature and mass flows of gases at the inlet were defined using CEL, based on a previous simulation with a full burner structure and finer meshes. Pressure boundary condition was set for the outlet. Heat transfer coefficient was applied for outside wall. In this case, it's set as 15 W/m^{2}K and the environmental temperature is set as 303 K.

Physical models

For the simulation of the turbulent flow in the furnace gas zone, the widely used standard $k-\epsilon$ model was applied. Eddy dissipation model [385] was used for the combustion of the natural gas with oxygen. This model is based on the concept that chemical reaction is fast relative to the transport processes in the flow. It is applicable in many industrial combustion problems where reaction rates are fast compared to reactant mixing rates. Radiation has a large contribution of the heat transfer to the scrap-salt zone and the furnace wall. Discrete Transfer Model (DTM) [385] was applied. The emissivity of the inner furnace wall and the interface between the gas zone and scrap-salt zone was set as 0.8. The buoyancy flow of the gas was simulated with the full buoyancy model implemented in ANSYS-CFX ®[385].

14.2.2 User developed sub-models

Population balance model for aluminium scrap melting

Population Balance Modelling (PBM) [386] (also see Appendix A.1.2 for details) is a very useful tool to represent the dynamic particle size variations as function of time, distributed physical properties and other process parameters. There are two forms of the population balance: A microscopic form and a macroscopic form. In this study, the simplified form of the microscopic population balance model was applied. The microscopic population balance model accounts for changes in a particle population in an infinitesimal volume at any geometrical position, as function of time. The general form of the microscopic population balance can be given by Eq. 14.7 (this is a different formulation than in Appendix A.1.2, given here to broaden the scope):

$$\frac{\partial \psi}{\partial t} + \frac{\partial}{\partial x}(v_x \psi) + \frac{\partial}{\partial y}(v_y \psi) + \frac{\partial}{\partial z}(v_z \psi) + \sum_{j=1}^{J} \frac{\partial}{\partial \zeta_j}(v_j \psi) + D - B = 0 \qquad (14.7)$$

Where $\psi = \psi(x, y, z, \zeta_1, \zeta_2, ..., \zeta_J, t)$ is the distribution of a property, as function of $x, y, z, \zeta_1, \zeta_2, ..., \zeta_J, t$; v_x, v_y, v_z are geometric velocities, $v_x = dx/dt, v_y = dy/dt, v_z = dz/dt$; $\zeta_j(\{\zeta_1, \zeta_2, ..., \zeta_J\})$ are a specified set of properties of the particles, $v_j = d\zeta_j/dt$ is the time rate of change of the property ζ_j; D is the death function of the property and B is the birth function of the property.

For the application of the population balance model for aluminium scrap melting, the form of PBM can be greatly simplified. There's no input or output during the melting process. The birth of new scrap pieces, due to break-up of the bigger ones, is difficult to obtain and assumed to be none, and there's no coalescence. Then the factors left are the shrinking (melting) and death of the scrap particles. For example, considering the scrap property of size, for a certain scrap particle, it shrinks during the process, transfers from a bigger-size group to a smaller-size group, and finally disappears. Furthermore, in the current process model, the scrap-salt zone was regarded as a conducting solid. The effect of fluid flow, furnace rotation and agitation was not taken into account directly, but represented by some model parameters, such as the Nusselt number for the scrap melting sub-model, the coefficients of effective thermal conductivity in the process model. The effect of geometric velocities can be omitted, thus, Eq. 14.7 can be simplified to Eq. 14.8.

$$\frac{\partial\psi}{\partial t}+\sum_{j=1}^{J}\frac{\partial}{\partial\zeta_j}(v_j\psi)+D=0 \tag{14.8}$$

where ζ_j can be the properties of the scrap such as size, shape and thermal properties. In the case of aluminium scrap melting, the population balance modelling of aluminium scrap size distribution is in fact the calculation of the melting rate of the aluminium scrap. The melting rate of a certain scrap particle is dependent on the position, time, local temperature, local Nusselt number, scrap properties etc., and it can be calculated by the user-developed melting sub-model, which was introduced in the next section.

Scrap melting model for a single aluminium particle

To calculate the melting rate of the scrap in such a two-melt (salt and aluminium metal) system in a rotary furnace, experimental study [387] and numerical modelling [384] was firstly conducted for a single aluminium particle melting in the molten metal and salt melts. The melting process of a scrap particle is dependent on the properties of the particle (such as the size, shape, composition, and initial temperature), the properties of the bulk melt (such as the temperature, liquid flow and agitation of the melt), and the situations when the particle was charged passing through the salt layer (such as the thermal properties of the salt melt, residence time in the salt layer and speed passing through the salt layer). If the scrap particle is regarded as a sphere with an original radius of R_0, energy conservation equations due to heat transfer in the system can be described as follows [388]. For heating of the sphere, when $0 < r < R_0$:

$$\frac{\partial T}{\partial t}=\alpha_p\left[\frac{\partial^2 T}{\partial r^2}+\frac{2}{r}\frac{\partial T}{\partial r}\right] \tag{14.9}$$

With initial and boundary conditions:

$$T=\begin{cases}T_0 & \text{if } r<R_0\\ T_{m,s} & \text{if } r=R_0\end{cases}\text{ at } t=0 \tag{14.10a}$$

$$\frac{\delta T}{\delta r}=0 \text{ at } r=0 \tag{14.10b}$$

$$\lambda_p\left(\frac{\delta T}{\delta r}\right)_{r=R_0-}=\lambda_{shell}\left(\frac{\delta T}{\delta r}\right)_{r=R_0+} \tag{14.10c}$$

where r is the particle radius, T is the particle temperature, t is the time, $T_{m,s}$ is the melting point of the shell, λ_p and λ_{shell} are the thermal conductivities of the sphere and the shell respectively, and α_p is the thermal diffusivity of the metallic sphere. Heat balance at $r = R_0$, the interface between the sphere and the shell, is expressed as the boundary condition in Eq. 14.10c. A shell is formed when a cold metal particle charged into a hot melt. For the shell development and re-melting, when $R_0 < r < R_{shell}$ Eq. 14.11 applies.

$$\frac{\partial T}{\partial t} = \alpha_{shell}\left[\frac{\partial^2 T}{\partial r^2} + \frac{2}{r}\frac{\partial T}{\partial r}\right] \tag{14.11}$$

With initial and boundary conditions:

$$R_{shell} = R_0 \text{ at } t = 0 \tag{14.12a}$$

$$T = T_{m,s} \text{ at } t = 0 \tag{14.12b}$$

$$T = T_{m,s} \text{ at } r = R_{shell} \tag{14.12c}$$

$$\lambda_{shell}\left(\frac{\partial T}{\partial r}\right)_{r=R_{shell}} = \rho_{shell}\Delta H_{shell}\frac{dR_{shell}}{dt} + h(T_f - T_{m,s}) \tag{14.12d}$$

where R_{shell} is the radius of the shell, ρ_{shell} is the density of the shell, T_f is the temperature of the bulk salt melt, ΔH_{shell} is the latent heat of the phase change, h is the heat transfer coefficient from the bulk melt to the solidifying shell, and α_{shell} is the thermal diffusivity of the shell. Heat balance at $r = R_{shell}$, the interface between the shell and the melt, is expressed as the boundary condition in Eq. 14.12d. If the bulk melt is changed during the process, e.g. an aluminium particle passing through the salt layer and entering the metal bath, there may be two shell layers formed. If the melting point of the sphere is higher than that of the shell, there will be no pre-melting of the sphere inside the shell. After the shell is re-melted, the metal solid sphere is further heated up and begins to melt. In this situation, the governing equation is the same as Eq. 14.9 but with different boundary conditions:

$$\frac{\delta T}{\delta r} = 0 \text{ at } r = 0 \tag{14.13a}$$

$$\lambda_p\left(\frac{\partial T}{\partial r}\right)_{r=R_{solid}} = \rho_p\Delta H_p\frac{dR_{solid}}{dt} - h(T_f - T_{m,p}) \tag{14.13b}$$

where R_{solid} is the radius of the solid core, ρ_p is the density of the particle, $T_{m,p}$ is the melting point of the metallic sphere, and ΔH_p is the latent heat of fusion of the sphere. Similarly, if the melting point of the sphere is lower than that of the shell, pre-melting of the sphere inside the salt shell may happen, then the boundary conditions of the governing equation, Eq. 14.9, can be expressed as follows, assuming that the temperature of the metal liquid inside the shell is unique and it equals the melting point of metal.

$$\frac{\delta T}{\delta r} = 0 \text{ at } r = 0 \tag{14.14a}$$

$$\lambda_p\left(\frac{\partial T}{\partial r}\right)_{r=R_{solid}} = \rho_p\Delta H_p\frac{dR_{solid}}{dt} + \frac{R_0^2}{R_{solid}^2}\lambda_{shell}\left(\frac{\partial T}{\partial r}\right)_{r=R_0} \tag{14.14b}$$

By solving these equations with a finite difference method [384], the melting process of a scrap particle under certain conditions can be simulated and the size change of the particle against heating time can be obtained. The melting behaviour of a metal particle as well as the salt shell formation and re-melting was studied. The results were compared with the previous

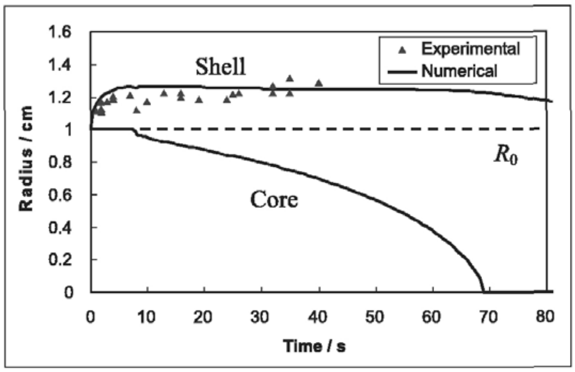


Figure 14.5: Experimental and numerical results of salt shell formation and re-melting on Al particles in molten salt bath

experimental study [387], and reasonable agreement was obtained. As an example shown in Figure 14.5, an aluminium particle, its equivalent radius is about 1.0 cm, was screwed on a steel rod, pre-heated to 280°C, dipped into the salt melt (NaCl-KCl 70%-30%wt base salt system, stagnant, 800°C) and then taken out after a certain immersion time. The weight and thickness of the salt shell formed on the aluminium solid was measured. The triangles in Figure 14.5 are the measured thickness of the salt shell, compared with the model prediction of the first 80 seconds. In this case, pre-melting of the aluminium core inside the salt shell happens, as shown in the figure. It should be noted that in this case, there's no metal melt in the system, because it's difficult to conduct and control the experiment when two melts exist. More details of the experimental study [387] and the numerical modelling [384] for aluminium melting as well as salt shell formation and re-melting can be found in the previous publications.

Implementation of the scrap melting sub-mode

For a multi-size particle system, the scrap is classified into certain groups depending on the scrap size. It can also be classified by other criteria, such as shape, composition, and scrap thermal properties, as well as the combinations of those criteria. For each cell in the scrap-salt zone, it is assumed that it has the same initial size distribution. A scrap melting sub-model was developed and integrated in the CFD based process model, it handles each size group the same as a single solid particle, calculates the melting rate based on the conditions in each cell in the scrap-salt zone at any time, based on the information exchange with the CFD framework. The melting sub-model provides the CFD framework with the information due to the melting of solid scrap, e.g. the heat sink due to melting, the amount of liquid metal and solid scrap, and the size distribution of scrap. At the same time, the CFD framework provides the information needed for the phase change calculations, e.g. the local temperatures. The scrap melting sub-model was simplified from the previous work of modelling a single particle melting in molten melts [384], in order to reduce the computing time. The fluid flow in the scrap-salt zone and the agitation due to furnace rotation were not fully included in the CFD based process model, and the re-solidification process was not simulated in the simplified melting sub-model and its effect on heat transfer were taken into account by some model parameters, such as the Nusselt number for the scrap melting model, the coefficients of effective thermal conductivity of the scrap-salt zone in the process model. Since the thermal conductivity of the aluminium metal is very high, the temperature difference within the particle can be ignored: $\delta T/\delta r = 0$. When the temperature of the solid particle reaches its melting point, the heat transferred from the environment to the particle is totally used for melting of the solid metal. The heat balance at the interface between the bulk melt and the solid, ($r = R_{solid}$) can be expressed by Eq. 14.15.

$$\rho_p \Delta H_p \frac{dR}{dt} = -h(T_f - T_{m,p}) \tag{14.15}$$

where the heat transfer coefficient, h, can be calculated based on the particle size, fluid flow condition and bulk melt properties, and the bulk melt temperature, T_f, can be obtained from the CFD simulations. Thus the size change of the particle can be calculated by Eq. 14.16.

$$dR = -\frac{h(T_f - T_{m,p})}{\rho_p \Delta H_p} dt \tag{14.16}$$

New particle size for each group in each cell and the total amount of melted particle in each cell at the current time step can be obtained. The heat sink for each cell due to phase change can be calculated and returned to the CFD framework as an energy source term, which influences the temperature distribution in the scrap-salt zone and heat transfer from the combustion gas or furnace wall to the scrap-salt zone. In this way, the melting rate of the scrap at any position and time can be obtained, and therefore the population balance of aluminium scrap melting can be established, based on the coupling of the scrap melting modelling and the CFD simulation of the furnace.

Development of the scrap burn-off sub-model

Aluminium is a very reactive metal, thus oxidation is always occurring during its life. In secondary aluminium process, the oxidized aluminium can never be reclaimed in secondary aluminium process and contributes to the losses. During the melting process, aluminium scrap is sometimes exposed in a high temperature and oxidation atmosphere, despite the presence of a protecting salt layer. The burn-off rate is dependent on the operation, salt amount, scrap quality and many other factors. The generated heat amounts to between 1/3 and 1/2 of the total energy input generated by burning of the natural gas [389]. This indicates that to build a valid process model, scrap burn-off must be taken into consideration. The scrap burn-off in composed of several different sources and reactions [389]. These reactions can be summarised as follows:

$$\mathrm{2Al + 3/2O_2} \rightarrow \mathrm{Al_2O_3} \tag{14.17}$$

$$\mathrm{2Al + 3H_2O} \rightarrow \mathrm{Al_2O_3 + 3H_2} \tag{14.18}$$

$$\mathrm{2Al + 3CO_2} \rightarrow \mathrm{Al_2O_3 + 3CO} \tag{14.19}$$

$$\mathrm{4Al + 3CH_2} \rightarrow \mathrm{Al_4C_3 + 3H_2} \tag{14.20}$$

$$\mathrm{2CH_2 + 3O_2} \rightarrow \mathrm{2CO_2 + 2H_2O} \tag{14.21}$$

It includes the direct oxidation reaction of aluminium metal, as expressed by Eq. 14.17, and the reaction between the aluminium metal and the moisture, as expressed by Eq. 14.18, or carbon dioxide, as expressed by Eq. 14.19. The aluminium metal also reacts with the contamination materials, e.g. plastic materials, and these reactions can also be regarded as the scrap burn-off, which generates a large quantity of heat and increase the metal loss, as expressed by Eq. 14.20, if the structural formula of the contamination materials can be approximately expressed as CH_2. Burning of the contamination materials and organic components attached on the scrap also has a similar effect on the melting process, as expressed in Eq. 14.21. Related to the distributed nature of the scrap, the scrap size distribution, surface to volume ratio, and content of contamination have a big influence of the scrap burn-off. For the scrap of "good" quality, which has a relatively small surface to volume ratio, less contaminations and/or higher metal content, the burn-off is normally less. And the total amount of scrap burn-off during the melting process is also influenced by a number of other variables in the system, e.g. temperature in the furnace, free-oxygen in the furnace, moisture content of scrap, melting status (liquid and solid ratio of metal). It makes very difficult to obtain the total amount of burn-off directly from the burn-off reactions and reaction kinetics. In this study, it was estimated by a mass and energy balance model with data reconciliation [389]. Data reconciliation is a technique by which the mass and energy balances can be closed by adjusting the measured data, while the measurements should be adjusted as little as possible. The adjusted data should give a more consistent representation of the actual process, which then forms the basis for any subsequent modelling that covers energy balances, statistics, kinetic modelling, neural nets and CFD modelling. For twenty-six furnace cycles, the burn-off rate for each furnace cycle was obtained through data reconciliation by closing the mass and energy balance as a function of standard deviation of errors in the measurements. These cycles were then split into three groups based on the properties of the scrap, and the calculated results are listed in Table 14.9[1] [389]. It indicates that for a certain type of the scrap feed, e.g. the scrap with a metal recovery rate of 80%, the scrap burn-off is 2.69%, and the heat generated due to scrap burn-off is about 657 MJ per ton of the scrap feed.

The scrap burn-off sub-model translates this part of heat, which contributes in both of the gas zone and the scrap-salt zone, into heat sources. It's too complex to consider all these factors by far and here only a simplified definition of the burn-off is present:

- Total amount of heat generated by scrap burn-off is pre-defined based on the mass and energy balance calculations [389], in relation to the scrap type and quality.

- Kinetics involved in burn-off was not taken into account yet, however this can be assumed to be rapid. The overall heat generation rate was defined based on the general industrial observations and the measured off-gas temperature, which can be used to indicate the extra heat generation in the furnace. Therefore a scrap burn-off function was defined with the function parameters roughly estimated based on a statistic calculation of several typical cycles. Figure 14.6 shows the pre-defined curve of the burn-off heat source together with the measured off-gas temperature.

- The scrap burn-off reactions and their following reactions generate heat both in the gas zone and the scrap-salt zone, while the ratio of the two parts is difficult to determine. It was thus studied as a model parameter.

- It is assumed that the burn-off reactions are position independent, and it's evenly distributed in the gas zone or in the scrap-salt zone.

- The effect of burn-off on the mass balance was ignored, which is very small.

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[1] Group 1: dross and Group 2: granules, shredder residue, turnings and Group 3: packages (bottle caps, cooling elements, turnings), shredder residue

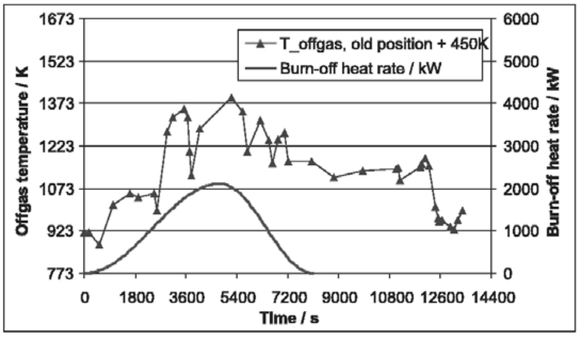

Figure 14.6: Pre-defined burn-off heat source (solid line), and the industrially recorded off-gas temperature

14.2.3 Results

General results

Turbulent fluid flow, gas combustion, radiation, and conjugated heat transfer in the rotary furnace were simulated in the CFD framework. The detailed information of the fluid flow in the gas zone, the temperature distribution in the furnace and energy flows of the process can be obtained. Figure 14.7 shows an example result of the flow in the gas zone and the temperature field in the furnace, at the 9600^{th} second of the process when about 80% of the scrap has been melted.

One of the main purposes of the simulation is to obtain the total melting time under a certain condition. Figure 14.8 shows the changing history of the total solids remaining, including the scrap and salt, against the heating time. It should be noted that the plotted remaining ratio are calculated by the total weight of the feed, which includes both scrap and salt. The melting curve can be regarded as the main criterion for the melting process, which indicates the time the scrap starts to melt and the time it has been melted completely. For melting of about 13 tons of scrap and 4 tons of salt flux, the total melting time is about 4 hours in this case, assuming that the burn-off rate is 2.7% and 50% of the burn-off heat (about 8540 MJ in total) contributes in the gas zone.

Influence of scrap size and shape

On the one hand, the experimental and numerical results [384] suggest that an aluminium particle with a larger size needs longer time to be melted. On the other hand, if the total weight of the feed is fixed, a combination with smaller sizes of scrap has a larger total surface area, which means more salt flux is needed in operation. Here, the melting sub-model has been developed and coupled with the CFD based process model. Population balance modelling of scrap with different size distributions can be established and the influence of the size distribution on scrap melting can be studied. The initial size distributions as well as their change during the melting process are shown in Figures 14.9 to 14.13. The distribution is plotted as the weight percentage to the total weight of scrap, against particle size, and the number of scrap groups is 25. In reality, the size distribution may be more complicated, dependent on the scrap type and the feed recipe. Here the initial size distributions studied are defined as follows:

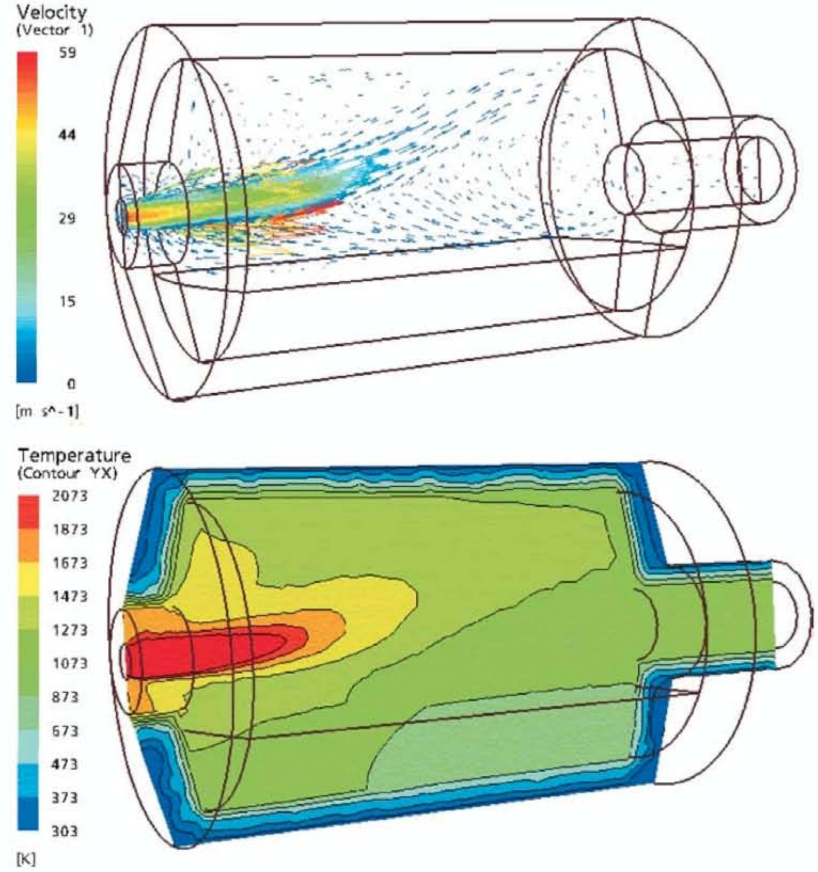

Figure 14.7: Flow in the gas zone and temperature field in the furnace at t=9600s

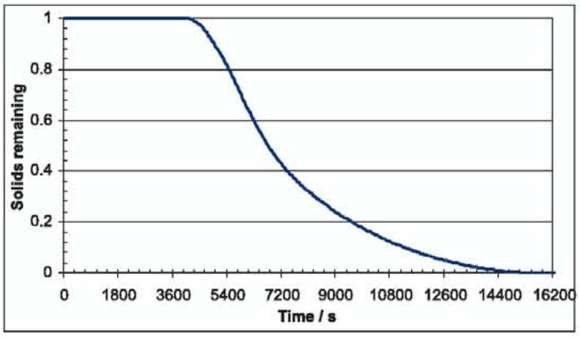

Figure 14.8: Melting curve of the solid (scrap and salt) in scrap-salt zone (ratio by total weight of feed)

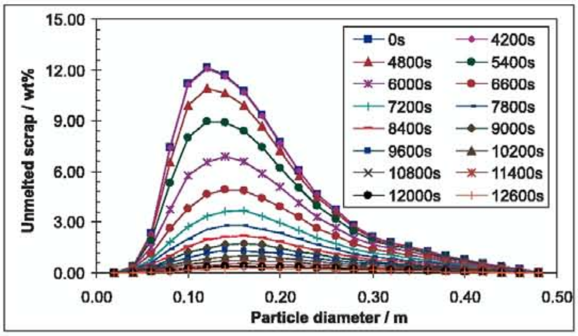

Figure 14.9: Simulated changing history of size distribution 1

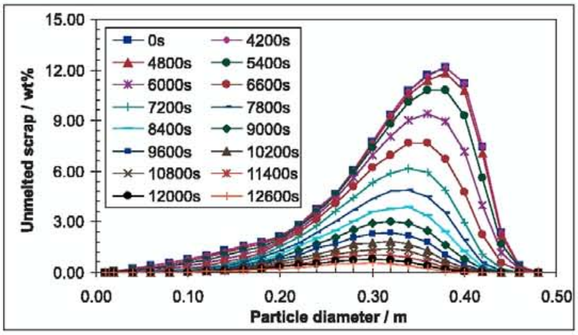

Figure 14.10: Simulated changing history of size distribution 2

- Size distribution 1: 0.0 m - 0.5 m in diameter, with a larger portion of smaller size of scrap.
- Size distribution 2: 0.0 m - 0.5 m in diameter, with a larger portion of bigger size of scrap.
- Size distribution 3: uniform size, 0.1 m in diameter.
- Size distribution 4: uniform size, 0.4 m in diameter.
- Size distribution 5: 0.0 m - 0.5 m in diameter, randomly distributed.

Figure 14.14 shows the melting curve of the aluminium scrap with different size distributions. For the scrap feed with larger portion of smaller particles (size distributions 3 and 1), the melting is faster than that with larger portion of bigger particles (size distributions 4 and 2) in the earlier stage. While the total melting time for all these cases is almost the same, about 14400 s (4.0 hours). It indicates that the melting process is mainly dependent on the heat transfer but scrap size. Here it should be noted that, in reality, scrap with smaller sizes normally has a lower metal recovery, causes a higher burn-off rate and requires more salt flux. These consequent effects have not been taken into account for these cases presented

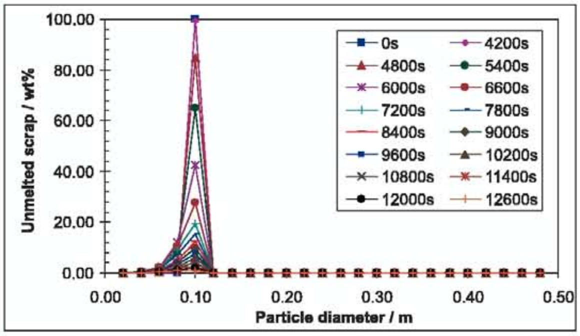

Figure 14.11: Simulated changing history of size distribution 3

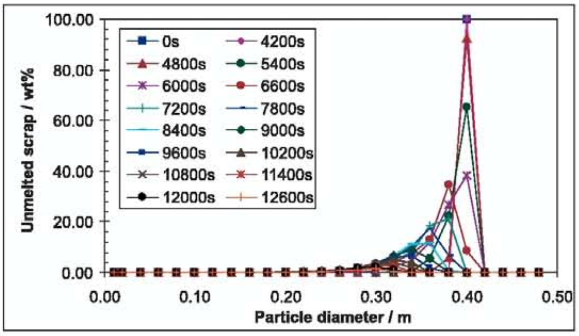

Figure 14.12: Simulated changing history of size distribution 4

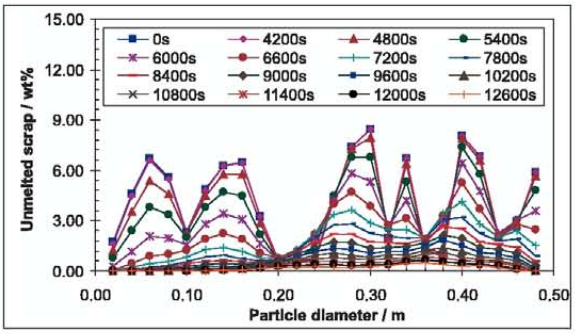

Figure 14.13: Simulated changing history of size distribution 5

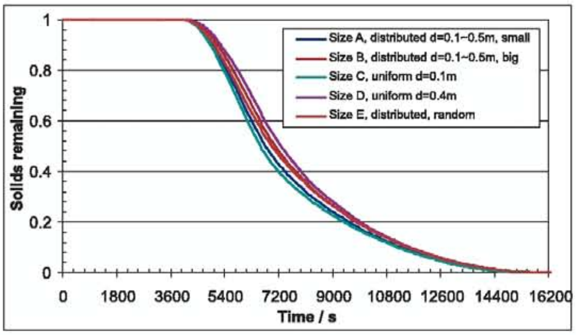

Figure 14.14: Melting curve of the solids in scrap-salt zone, with different size distributions

here. The aluminium scrap also has a large variety of shapes. The shape factor was applied and defined as the ratio of the surface area of the particle to the surface area of a sphere with the same volume, e.g. it's 1.0 for the spheres and it's 1.24 for the cubes. The results indicated that there's little influence of the shape, the shape factor ranges from 1.0 to 20.0, if other parameters are not changed. While in reality, larger surface area to volume ratio of scrap would result in a larger requirement of salt flux, which may influence the scrap melting process.

Influence of scrap quality

Metal burn-off during the melting process is one of the main reasons of metal loss in secondary aluminium, while it also generates a large amount of heat. According to the observations and data measurements in the plant, as well as the mass and energy balance calculations, the scrap burn-off rate has an obvious relationship to the scrap type or scrap quality [389]. Normally, for the "good" quality of scrap, which has a relatively small surface to volume ratio, less contamination and/or higher metal content, the metal recovery rate is higher and the metal loss is normally less. The burn-off model is only implemented preliminarily, chemical reactions and their mechanisms are not taken into account, and here the study is focused on the energy aspect. For a total input of 13 tons of scrap feed, the scrap melting behaviour was simulated with different scrap burn-off rates, 0.0% (A, no burn-off), 1.5% (B), 2.0% (C), 2.7% (D) and 3.5% (E), and the heat generated in total is 0 MJ, 4750 MJ, 6330 MJ, 8540 MJ and 11070 MJ respectively. It assumes that the heat generated in the gas zone and that in the scrap zone are the same, 50% to 50%. Figure 14.15 shows the melting curves for these cases. The total melting time is about 6.25 hours, 5.25 hours, 5.0 hours, 4.35 hours, and 3.5 hours respectively, which indicates that the total amount of burn-off has a big influence on scrap melting. A higher burn-off rate results in a shorter melting time, but it is at the expense of metal loss.

The generated heat due to scrap burn-off contributes both in the gas zone and the scrap-salt zone, as discussed in the previous paragraphs, while the ratio of these two parts is difficult to decide. It was studied as a parameter in the model. Figure 14.16 shows the melting curves with different ratios of the heat contributed in the gas zone and the scrap-salt zone, 0%, 20%, 50%, 80% and 100% in the gas zone respectively. For the same scrap burn-off rate, 2.7% here, larger ratio in scrap-salt zone results in a faster melting of scrap. For these cases, the total melting time ranges from 4.0 hours to 4.5 hours.

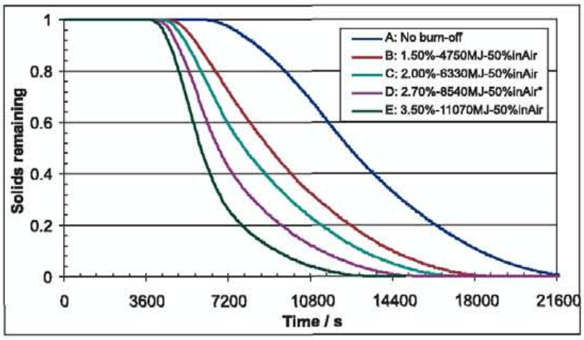

Figure 14.15: Influence of the scrap burn-off rate, the total amount

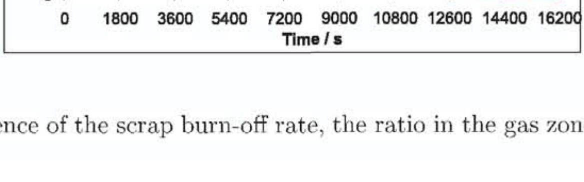

Figure 14.16: Influence of the scrap burn-off rate, the ratio in the gas zone and the scrap-salt zone

14.2.4 Discussion of CFD model

A CFD based process model was developed, in which fluid flow, heat transfer, natural gas combustion, and radiative heat transfer were simulated for the scrap melting process. Data measured in industry were applied in the model as initial and boundary conditions, as well as for model validation. User sub-models for scrap melting and scrap burn-off were developed and integrated into the CFD framework. A simplified population balance model for aluminium scrap melting was established by classifying the scrap feed into some scrap groups. The melting rate for each group in each cell at each time step was calculated with the exchange of information between the melting sub-model and the CFD based framework. Thus the distributed nature of the complex scrap feed can be taken into account. The distributed properties of scrap also result in distributed burn-off rates. The scrap burn-off sub-model was developed to take into account the influence of the burn-off heat on the scrap melting process. Various case studies were carried out focussing on the relationship between the melting process and the scrap properties, e.g. scrap size, shape, burn-off and quality. It shows that the scrap size and shape only have a small influence on melting, if ruling out the other consequent effects due to size and shape difference. The distributed burn-off rate, which represents the scrap quality here, is one of the important factors for the melting process. For the scrap with a higher burn-off rate, which normally is the scrap with a "poor" quality, the total melting time and the gas consumption can be reduced, while it's at the expense of more metal loss. The melting sub-model can be further improved, e.g. taking consideration of the re-solidification [384], and refining the model parameters. The scrap burn-off sub-model can also be improved by refining the burn-off function, taking into account the chemical composition, distributed kinetics, etc. Moreover, the sub-models are not completely coupled with each other yet, e.g. the scrap burn-off rate has not been directly related to the distributed scrap properties but pre-defined, which should be improved in the future.

Appendix A

Fundamentals of physical separation and metallurgical recycling

This section discusses various relevant theory underpinning the various developed theory discussed in the main body of this book. Examples by the authors are also presented here to illustrate in theoretical depth various aspects of this book. Furthermore, the concept of property is discussed and showing the connection between the property, mass balancing and the possibility to use property classes in population balance models of both physical separations and in larger sustainability cycle estimations.

A.1 Particulate recycling systems

Particles in particulate solids can be defined by their properties. The most important of these properties must be understood in order to be able to design and operate physical, metallurgical and other chemical separation and beneficiation processes for recycling and to model material cycles for sustainable development. Properties like size; density, form, magnetic susceptibility, colour and concentration of a chemical substance can be mentioned as direct physical and chemical properties. The property can also be indirect like floatability or degree of liberation. A property can also be defined in economical or ecological terms. The property discontinuity allows us naturally to present the property in classes. The number of classes and the width of a class can be defined freely and will depend on the goals of modelling and the accuracy we want to achieve.

A.1.1 Sampling

The sampling of recyclable and recycled material is a special kind of particulate sampling. A starting point for sampling is the discontinuous nature of the property we are interested in. The "errors" taking place in the sampling and in the related analysis, will depend on the number of particles we analyse. An important feature due to the discrete nature of the property is that the property can be spatially distributed. As has been argued in the previous chapters, an estimate of the property and its variance are important for data reconciliation and all modelling described in the book.

- The variance of a single primary increment is composed of the variance of the material (fundamental error), the sampling variances and the analytical variance.
- The variance of the material property is for the mean of n primary increment measurements n time smaller than the variance of a single increment.
- The variance of the material property in a primary increment of mass m is m times smaller than in a 1 kg sample increment.
- The variance of sample treatment and analysis for the mean of k samples is k times smaller.

These come from the central limit theorem:

$$\sigma_{\bar{x}} = \frac{\sigma}{\sqrt{n}} \tag{A.1}$$

The Gy sampling model is the most used for all particulate applications like recycling sampling. According to Gy the variance of the fundamental error is:

$$\sigma^2_{fe} = \left(\frac{1}{M_s} - \frac{1}{M_L}\right) c \cdot l \cdot f \cdot g \cdot x^3 \tag{A.2}$$

where:

M_s	sample mass
M_L	mass of the lot to be sampled
c	mineralogical composition parameter
l	liberation parameter
f	shape parameter of a particle
g	size range parameter
x	the maximum particle size (95% passing!)

Often the term $c \cdot l \cdot f \cdot g \cdot$ is called the Gy [390, 358] constant and denoted as C. There are very few studies of the effects of the liberation, shape and composition parameters when sampling scrap. The equation can be used to estimate the sample size if the confidence interval E_s is defined.

$$E_s = + \frac{t \cdot \sigma_p}{\sqrt{n}} \tag{A.3}$$

where t is the student t-value with the required confidence limit and (n-1) degrees of freedom. For variables that are functions of other variables:

$$y = f\left(x_1, x_2. ..., x_k\right) \tag{A.4}$$

the variance of (y) has to be written as:

$$Var\left(y\right)=\left(\frac{\partial y}{\partial x_1}\right)^2\cdot\mathrm{var}\left(x_1\right)+\left(\frac{\partial y}{\partial x_2}\right)^2\cdot\mathrm{var}\left(x_2\right)+...+\left(\frac{\partial y}{\partial x_k}\right)^2\cdot\mathrm{var}\left(x_k\right)\qquad(A.5)$$

Example A.1

Computing the joint effects of variances.

Calculate the confidence limits of the amount of metal (m) in a lot of Al scrap.

The lot was weighed to be 5500 tons with a moisture of 2.8% and Al assay (c) 38.8% Al. The relative error of the weighing (w) was 1.9%, the relative error of the moisture measurement was 6.5% and the relative error of the assay 2.8%.

The means, relative errors and variances are

Variable	Mean	Relative error	Variance
Mass	5500 ton	1.9%	10920
Moisture	2.8%	6.5%	0.0331
Al Assay percentage	38.8%	2.8%	1.180

Forming the equation corresponding to Eq. A.4 we get by using solids content (s) instead of moisture:

$$m = wsc$$

Writing and substituting the partial derivatives gives:

$$Var\left(m\right)=\left(sc\right)^2\cdot\mathrm{var}\left(w\right)+\left(wc\right)^2\cdot\mathrm{var}\left(s\right)+\left(ws\right)^2\cdot\mathrm{var}\left(c\right)$$

The means, relative errors and variances are now:

Variable	Mean	Relative error	Variance
Mass	5500 ton	1.9%	10920
Solids content	0.972	0.188%	$3.31\cdot10^{-6}$
Al Assay fraction	0.388	2.8%	$1.18\cdot10^{-4}$

By substituting these estimates of the means and corrected variances to Eq. A.5 one obtains get:

Variable	A (Partial derivative^2)	B (variance)	AB
Mass	0.1422	10920	1553
Solids content	4554000	$3.31\cdot10^{-6}$	15
Al Assay fraction	28580000	$1.18\cdot10^{-4}$	3373
TOTAL SUM			4941

The mean for the Al tonnes is simply by multiplication 2074 tonnes and the standard deviation for the Al tonnes in the lot 70.3 tonnes. The 95% confidence limit of the metal content is 2074±138 tonnes. It is easily seen that the relative error of the assay is responsible for 68% of the final total variance. It is also obvious that no extra work should be spent on the moisture analysis.

A.1.2 Population Balance Modelling (PBM)

The distributed nature of material streams has been made clear in various chapters of this book either by suitable photos or by relevant theory. This chapter will give a short overview on the relevant theory of Population Balance Modelling (PBM) [391, 392, 334, 393].

Mathematical modelling has proved to be a very successful approach for improving the design and performance of mineral and metallurgical processes. Mineral processes almost invariably involve particles, as solid fragments, liquid drops or bubbles. Process performance is usually highly dependent on the behaviour of these particles. Particulate system analysis simulates the behaviour of the population of particles and its environment from the behaviour of single particles in their local environment [334]. It is more valid to consider particulate systems separately instead of as a bulk phase system. Often a few independent properties, like temperature, composition, rate or equilibrium relations are enough to characterise a bulk phase system. Particulate systems need additional information to adequately describe them. Such a need for additional information arises from the fact that each individual particle can be given different values for those properties.

For example, consider an aluminium particle. Its surface area and hence its size determines the degree of oxidation and hence the metal loss as aluminium oxide. It also determines the rate at which it melts. Furthermore, surface tension also affects the melting behaviour and losses as do surface coatings. Furthermore, the behaviour of particles during shredding are described in Chapter 9, without as yet going into the detail of material liberation. In fact PBM is used to describe the change of particle size as the material / end-of-life products flow through a shredder.

Property space

The properties form an $\Re^n$ space. We can define a sub-space of the general space having the chosen properties and the subsequent dimensionality $m(m < n)$. Choice of coordinates $x_{i...m}$ is dictated by the demands of the model(s). A particulate will belong to a class of all the chosen properties. Each point of this space $x_{ijk...m}$ represents a combination of the defined values of the m properties chosen to represent the particles. In case we are using discrete classes for the properties a volume in the space $x_i, x_j, x_k, ..., x_m$ will represent the point. We denote this volume to be region $\Re_e$.

The number fraction of the entire particle population that occupies unit volume $\Re_e$ of the particle phase space is called the generalized particulate number distribution density function $\Psi(x)$.

$$\Psi_{ij...k}\left(x_{(1)i}, x_{(2)j}...x_{(n)k}\right) = \int\limits_{X_{(1)i}}^{X_{(1)i-1}} \int\limits_{X_{(2)j}}^{X_{(2)j-1}} ... \int\limits_{X_{(n)k}}^{X_{(n)k-1}} \psi\left(x_{(1)}, x_{(2)}...x_{(n)}\right) \cdot dx_{(1)} \cdot dx_{(2)} \ldots dx_{(n)} \qquad (A.6)$$

The number distribution function can be calculated for discrete property classes as well. Obtaining number based data is however often very difficult or even impossible. Therefore a transformation to a mass-distribution is often required. Population balance models describe the change of a population (property class) as a function of time. They are a special class of process dynamic models. Models can be formulated both for continuous and discrete property functions. They can also be formulated for time continuous or for discrete events. As the measurements of most of the properties a particle assembly can have, produce discrete property

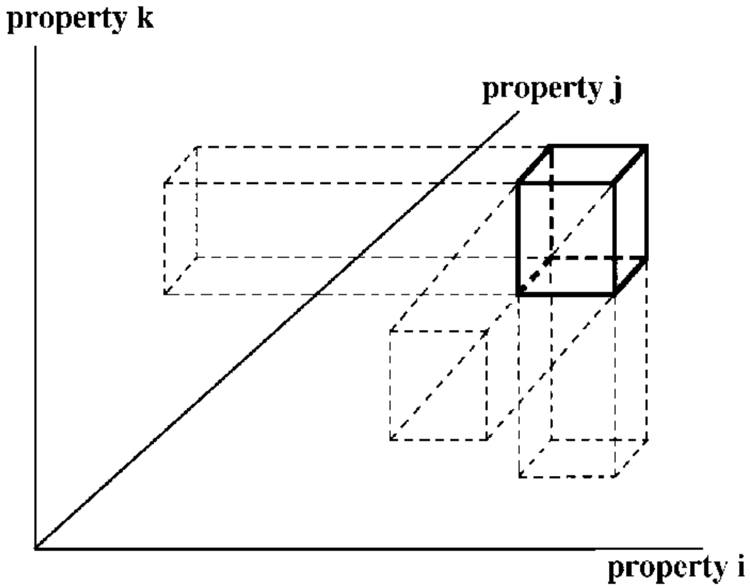

Figure A.1: A property space $\Re^3$ and region R_c

functions, the property discrete models are often used. The choice between time continuous and time discrete must be made according to the recycling process we are dealing with. Referring to the region R_c in Figure A.1 King [334] has formulated the different processes by which a particle in the property space region R_c can move to another region. The movement across the boundaries of R_c can take place as:

- convective "motion" in phase space through the boundary S_c of the volume R_c,
- arrivals by finite steps from other regions in the phase space; birth,
- destruction of particles in region R_c, and
- physical additions and withdrawals of particles having the same internal coordinates.

Changes in the number or mass of particles in the specific region R_c can be obtained by:

$$\frac{\partial}{\partial t}\int\limits_{R_c} N \cdot \Psi(x)\, dx = -\int\limits_{S_c} N \cdot \Psi(x) \cdot u \cdot \mathbf{n} \cdot d\sigma - D + B - Q + A \tag{A.7}$$

(x)	particulate (number) distribution function
u	vector of "velocity" at which particulates change phase coordinates
N	number of particles in the system
n	outward pointing normal vector at surface S_c
S_c	the surface enclosing region R_c

$B\&D$	rate of birth and destruction of particles respectively
$A\&Q$	rate of addition and removal (through product input and output streams) respectively

The surface integral must be changed to a volume integral by applying Green's theorem, through which Eq. A.8 is obtained.

$$\frac{\partial}{\partial t}\int\limits_{R_e} N\cdot\Psi\left(x\right)\cdot dx-\int\limits_{R_e} N\cdot\nabla u\cdot\Psi\left(x\right)\cdot dx-D+B-Q+A \tag{A.8}$$

This equation forms the basis for population balance models. General equations can be written for the different parts of the equation. Examples demonstrate how the model can be adapted for the solution of different recycling problems; either local separator performance troubleshooting or larger systems like car recycling in Europe.

Modelling the melting of steel scrap

The population balance is simply a way to account for the number of things. In general terms these "things" are called entities. For recycling the entities are metal and material particles. In the population balance, the entities are then accounted for (balanced). Starting with a certain number of particles, there should be the same number at the end - unless some are removed - or some are added, or the ones that have been kept change in number, e.g. they have aggregated or have broken. The number of entities is influenced by inflow and outflow of the system and by processes happening to the entities within the system. These (internal) processes are called "birth" and "death" processes, which respectively increase or decrease the numbers. Quantifying these internal processes is the most difficult part in applying population balance methods.

The First Step: The Simple Population Balance Model In order to simulate the melting of steel scrap particles in a molten bath of a melting reactor (converter or ladle) depicted by Figure A.2 then the population balance model (PBM) is described as follows:

$$\frac{dN\left(t\right)}{dt} = n_I\left(t\right)-n_E\left(t\right)+B\left(t\right)-D\left(t\right) \tag{A.9}$$

$$\frac{dN}{dt} = n_I-n_E+B-D \tag{A.10}$$

where:

N	number of particles in a base element
n	number of particles in a base element
B, D	Birth or Death function i.e. creation of new particles or disappearance of particles

However, this equation is not complete. Ageing should be included. Ageing influences the distribution of the property considered without influencing the total number count [1]. It can

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[1] For example, dissolution and abrasion of particles are ageing functions: during dissolution or abrasion, the total number of particles is not altered

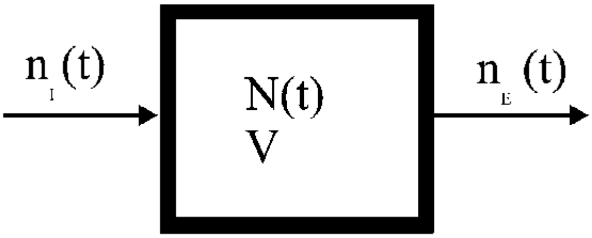


Figure A.2: A scrap melting furnace (convertor)

be formulated using the cumulative distribution function $F(x,t)$ or density function $f(x,t)$. First, the PBM for particle sizes smaller than x (no ageing) is as follows:

$$\frac{\partial(NF)}{\partial t} = n_I F_I - n_E F_E + BF_B - DF_D \tag{A.11}$$

where:

F	cumulative particle size distribution function
f	particle size density distribution function

Including the ageing or growth function $G(x,t)$ gives the following equation:

$$\frac{\partial(NF)}{\partial t} = n_I F_I - n_E F_E - NG\frac{\partial F}{\partial x} + BF_B - DF_D \tag{A.12}$$

Under the following simplifying assumptions:

- Isothermal
- Steady state:
$$\frac{\partial N}{\partial t} = 0,\ \frac{\partial n_I}{\partial t} = 0,\ \frac{\partial n_E}{\partial t} = 0$$
- Well mixed: $F = F_E$
- No birth or death: $B = 0$ and $D = 0$
- One property: size x
- F_I = *Rosin-Rammler* distribution
- One ageing or growth function: the melting of scrap particles
- All particles are spheres

Eq. A.12 will be reduced to:

$$N\frac{\partial F}{\partial t} = n_I F_I - n_E F - NG\frac{\partial F}{\partial x} \tag{A.13}$$

The Second Step: Ageing or Growth Function: Scrap melting The melting of steel scrap particles with size x, is determined by the scrap alloy composition, the melt composition, the temperature, and the mass transfer coefficient. For a one spherical particle system the following equations hold [394]:

$$\frac{dx}{dt} = -k_C \cdot \frac{\left[C_C^B - C_C^L\right]}{\left[X_C^L - X_{C,s}^o\right]}\left(\frac{M_{Fe}}{\rho_s^o}\right) \tag{A.14}$$

$$\frac{dc_x}{dt} = -4 \cdot \pi \cdot x^2 \cdot k_C \cdot \frac{\left[C_C^B - C_C^L\right]}{\left[X_C^L - X_{C,s}^o\right]} M_{Fe} \tag{A.15}$$

(A.16)

where:

c_x	dissolved mass of steel scrap from particle with size x [kg]
x	particle size [m]
$\rho_s crap$	density of scrap [kg m^3]
k	dissolution rate constant, mass transfer coefficient [m s 1]

For the scrap melting of all particles with size x, with given density distribution f, the following equation can be derived:

$$C_x = N \cdot f(x) \cdot c_x = N \cdot c_x \cdot \frac{\partial F(x)}{\partial x} \tag{A.17}$$

Integrating over the complete particle size range will give the scrap melting for the complete particle size distribution PSD:

$$C_T = \int\limits_{x=0}^{x=\infty} c_x N f(x)\, dx \tag{A.18}$$

Considering this for the complete PSD with the known distribution ($Forf$), the change in particle size becomes:

$$N \cdot f(x) \cdot dx = \frac{N \cdot f(x)}{4 \cdot \rho_{scrap} \cdot \pi \cdot x^2} dc_x \tag{A.19}$$

The Third Step: The Particle Size Distribution The *Rosin – Rammler* distribution will be used in completing the set of equations for the PBM. The density distribution of the PSD is given by Eq. A.21 and the cumulative distribution of the PSD by Eq. A.20, f being the derivative of F:

$$F(x) = 1 - e^{\ b \cdot x^n} \tag{A.20}$$

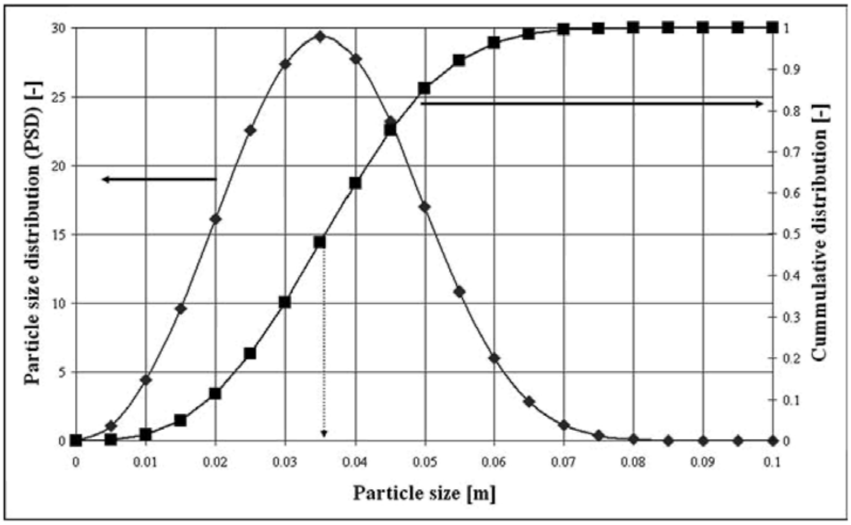


Figure A.3: Rossin-Rammler: Particle size distribution PSD f and Cummulative distribution function F *(a=3.0216 and b=16377)*, which is also the separability function ζ

$$f(x) \quad = \quad a \cdot b \cdot x^{a-1} e^{-b \cdot x^{a}} \tag{A.21}$$

One of the first assumptions is the distribution of the particles entering the base element. The assumption is that the mean diameter (d50) is 0.036 m (36 mm) and the standard deviation is 0.013 m (13 mm)15. For the particles entering the base element, a_I is 3.0216 and b_I is 16377. The distribution functions are illustrated in Figure A.3.

The Fourth Step: Completing the Balance The total scrap melting of all the particles with size x is:

$$N \cdot f(x) \cdot c_x \tag{A.22}$$

The simple PBM (Eq. A.13) then becomes:

$$N \cdot \frac{\partial F}{\partial t} \quad = \quad n_I \cdot F_I - n_E \cdot F - N \cdot G \cdot \frac{\partial F}{\partial x} \tag{A.23}$$

$$or$$

$$N \cdot \frac{\partial f}{\partial t} \quad = \quad n_I \cdot f_I - n_E \cdot f - N \cdot \frac{\partial (G \cdot f)}{\partial x} \tag{A.24}$$

$$noting \frac{\partial F}{\partial x} \quad = \quad f$$

Here the growth or ageing function, G, is the melting rate (in this case) of a property for a single particle:

$$G = \frac{dx}{dt} \tag{A.25}$$

$$N \cdot \frac{\partial F}{\partial t} = n_I \cdot \left(1 - e^{-b_i \cdot x^{a_i}}\right) - n_E \cdot F - \left(N \cdot G \cdot \frac{\partial F}{\partial x}\right) \tag{A.26}$$

(A.27)

The mass transfer rate, k, in Eqs. A.15 and A.16 is obtained according to suitable mass transfer correlations. [394]

Modelling a shredder

Under the following simplifying assumptions for a shredder, Eq. A.12 will be reduced to Eq. A.28.

- Steady state:
$$\frac{\partial N}{\partial t} = 0, \ \frac{\partial n_I}{\partial t} = 0, \ \frac{\partial n_E}{\partial t} = 0$$
- Well mixed: $F = F_E$
- One property: size x
- F_I = *Rosin-Rammler* distribution

$$N\frac{\partial F}{\partial t} = n_I F_I - n_E F - + BF_B - DF_D \tag{A.28}$$

The B and D functions are still a daunting task to create, however, some effort is being done in this regard as discussed in Chapter 9.

A.1.3 Physical Separation basics

The variables affecting the outcome of physical separations in recycling are related to the material properties and their distribution and to the process dynamics, separator operation and design. In separation a suitable action (force) is generated and applied to the particles. The choice of this force will depend on the property to be exploited. It can be any physical or surface chemical property. To mention a few, materials can be separated according to their size, density, susceptibility, colour etc. The forces affecting a particle are balanced in such a way that those particles having the property will report to different product than those that do not possess the property or level of property (reject). The reject fraction refers only to particles having not responded to the separation force and does not include any allusion to other values. For example in a sink float separation particles are floated in a medium with a given density. Some particles have a higher density and will sink (accept fraction) while others have a lower density and float (reject fraction).

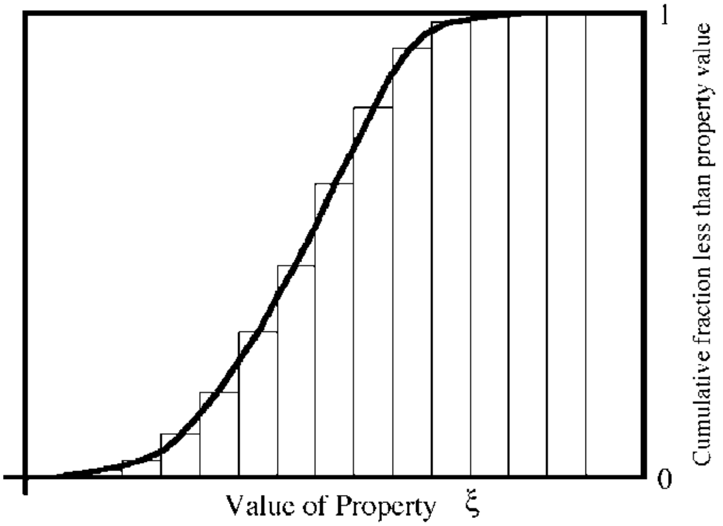


Figure A.4: Separability curve

Separability

A separation process ideally exploits only one property at a time but in practice this is not achieved. Due to the relative movement of particles in a fluid and the absolute movement of the fluid, the absolute velocities towards accepted or rejected products depends also always on particle size. Properties are often also interdependent. The material flow to be separated may consist of a single solid phase or more often from multiple solid phases. In the former case the separation aims at separating at some set point in order to improve the economic value of the product by rejecting some particles with low property value. In the latter case all phases will have a distribution of the property. The properties of different solid phases may overlap like the density of various plastics. The cumulative form of the exploited property variation is called the separability curve. The property can vary due to internal material heterogeneity (surface or volume), incomplete liberation or differing manufacturing or earlier history of the particles. Figure A.4 gives a separability curve of property ζ. Separability curves can be measured by changing the variable affecting property ζ in a laboratory experiment or in a batch separator.

Especially in situations where larger particles are made of multiple solid phases the separability curve is also a function of particle size. It has to be remembered that the separability curve is not the same as the separation efficiency curve. The former is purely a distribution of property and the latter describes the functioning of a separator.

Grade/recovery

The simplest separation stage is according to Figure A.5. The "accept" stream is the one, which is more affected by the force used by separation.

All separations of recycled materials can be characterised by mass efficiencies or by a

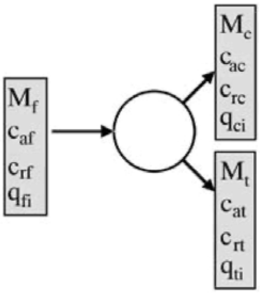


Figure A.5: Simple two-stream separation

property class based distribution efficiency. A simple and obvious way is to express the efficiency by relating the mass flow rate of a separated product stream to the feed stream. Separation efficiency E_o can be given as a relation between the product (concentrate) stream (c) and the feed stream (f) as defined by Eq. A.29.

$$E_c = \frac{M_c}{M_f} \tag{A.29}$$

If the relation is done with the reject stream (t) we talk of total efficiency E_t, which is $1 - E_c$. The total efficiency can be determined from property class data (frequency or cumulative). For reconciled data Eq. A.30 can be derived.

$$E_t = \frac{Q_{fi} - Q_{ti}}{Q_{ci} - Q_{ti}} = \frac{q_{fi} - q_{ti}}{q_{ci} - q_{ti}} \tag{A.30}$$

The ratio between the reject mass flow M_u and the product mass flow M_o is important. It is called circulation ratio C (or commonly, misleadingly, circulating load) and is defined by Eq. A.31.

$$C = \frac{M_t}{M_c} \tag{A.31}$$

The most common mass efficiency measure is the recovery R given as a percentage. It is defined for a two-stream separation (Figure A.5) at a point of interest (property value / class).

$$R = 100\frac{M_c Q_c}{M_f Q_f} \tag{A.32}$$

Recovery can also be given using property class values. Often chemical assays are used instead (notation of Figure A.5).

$$R = 100\frac{c_{af}\left(c_{ac} - c_{at}\right)}{c_{ac}\left(c_{af} - c_{at}\right)} \tag{A.33}$$

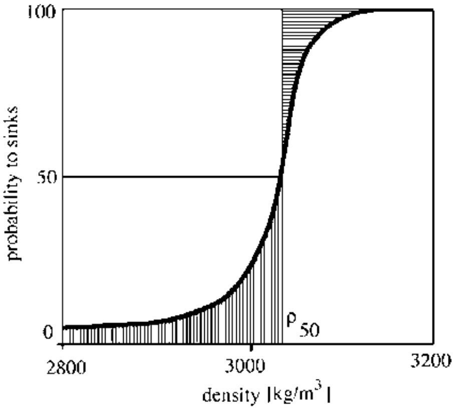


Figure A.6: Misplaced particles in a density separation

As recovery describes the fraction of valuable / interesting material reporting to the product flow, it has its major use in economic calculations and in day-to-day operations. The equation should not be used with raw data as the term $(c_{af} - c_{at})$ contains values that often are of the same order of magnitude. Considering each property class (i) separately, we obtain an understanding of separator performance, which is much more detailed and can be used as a basis for separator comparison and separator modelling. The separation efficiency curve can be constructed (Heiskanen [333] by plotting the fractional probabilities (recoveries) of each property class (i) that are to go to the reject (tailings) stream (t) as defined by Eq. A.34 against the property class value (Figure A.6). In Figure A.6 the shaded areas show which the particles that are misplaced. The lower shaded area gives the fraction of particles going to the "accept" fraction instead of the "reject" fraction where they belong. The upper shaded area describes those particles that for some reason go to "reject" instead of "accept". The misplaced particles decrease the quality of the respective product.

$$Y_i = 100 \frac{M_t}{M_f} \frac{q_{ti}}{q_{fi}} \tag{A.34}$$

Grade-recovery curve

Adding cumulatively classes of property ζ of the "accept" product and plotting the respective grade vs. recovery defines the theoretical Grade-Recovery curve (Figure A.7). As with separability we can distinguish the theoretically obtainable Grade-Recovery curve and the technical grade-recovery curve obtained with a given separator (process) under given operating conditions. The calculation of this is shown by the following example.

Example A.2
Grade recovery curve

Let the measured performance of a separation be given by the data in Table A.2.

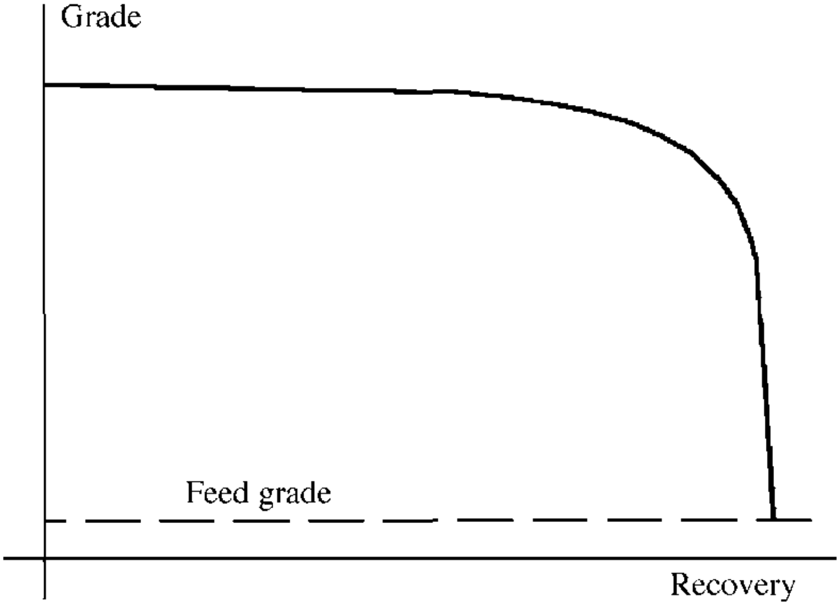


Figure A.7: Grade-recovery curve (feed grade implies 100% recovery i.e. the complete feed is recovered)

Table A.1: Data for determining the Grade-Recovery curve of a separation unit

Property class	Class mean of property ζ value	Feed (mass)	Product "accept" (mass)	Grade efficiency
1	95	17.23	17.23	100.0
2	85	12.56	12.48	99.4
3	75	9.29	9.10	97.9
4	65	5.18	4.90	94.5
5	55	2.65	2.15	81.1
6	45	3.43	1.77	51.7
7	35	6.55	1.60	24.4
8	25	13.11	1.84	14.0
9	15	34.67	3.87	11.2
10	5	54.77	5.79	10.6
total		159.44	60.72	

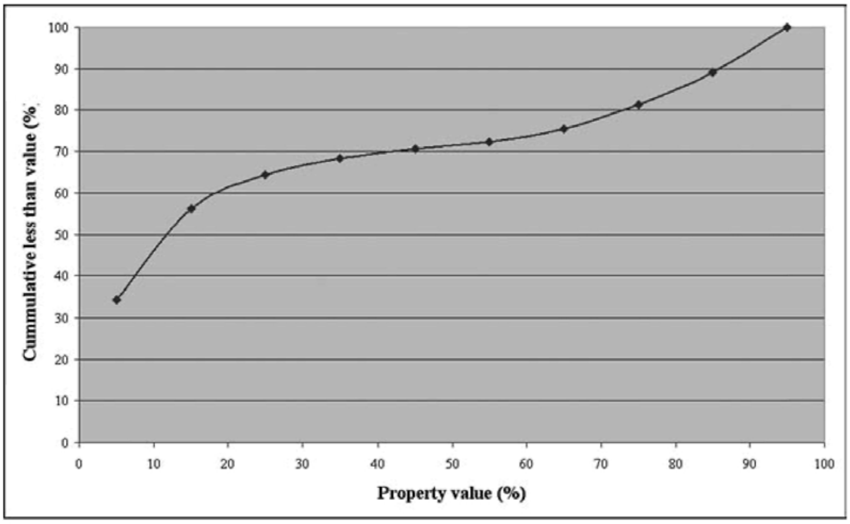


Figure A.8: Separability curve for feed

$$\text{Average}_{\text{Property class}} = \sum_{\text{All classes}} \text{Property class} \cdot \text{Fraction}_{\text{Property class}}$$

from which follows feed grade 33.8% and product grade 67.3%, mass recovery 38.0% and recovery 75.8%. The separability curve of the example is given by Figure A.8. The related grade efficiency curve is is given by Figure A.9. The theoretical grade- recovery curve is deduced from the feed property classes (separability) and depicted by Figure A.10.

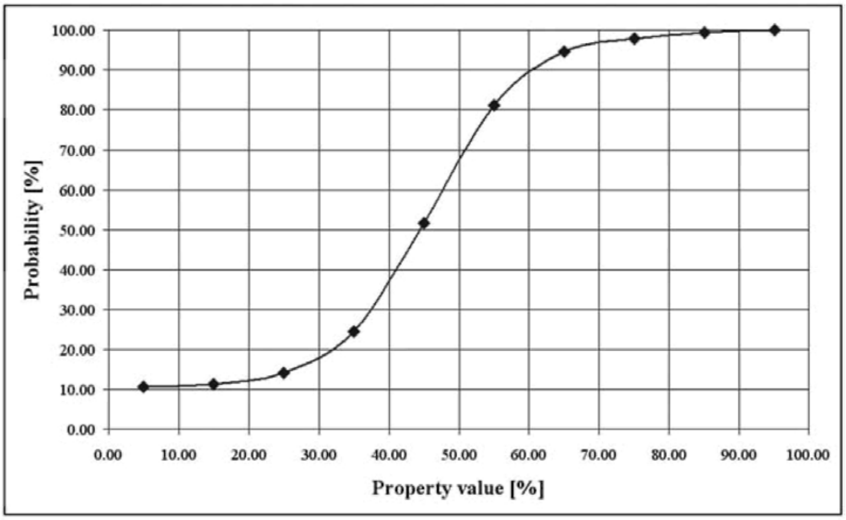


Figure A.9: Grade efficiency curve (column 4 in Table A.2)

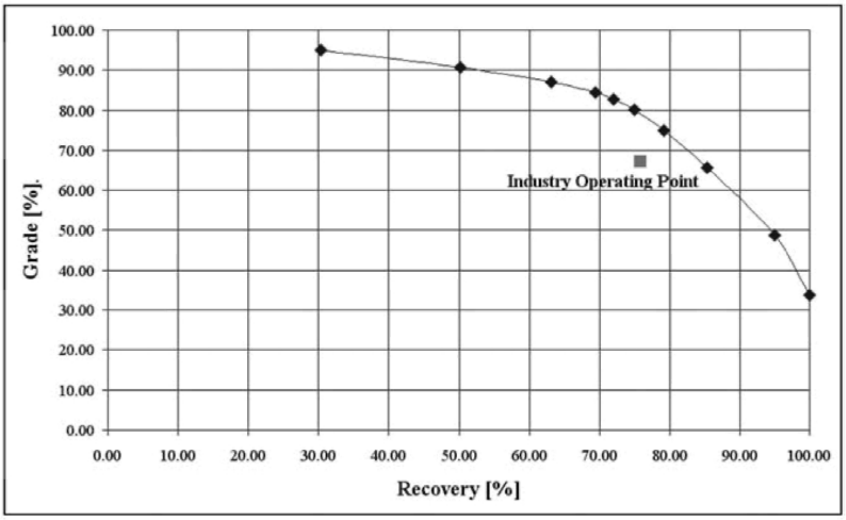


Figure A.10: Grade-recovery curve derived from data in Figure A.8 by progressively calculating the new grade and recovery as the cumulative size fractions are recovered starting with the initial grade of 95% of the first fraction and its fractional recovery and ending with 100% recovery for the weighted average grade of all classes; with industrial operating point superimposed

A.2 Thermodynamics of recycling metallurgy

Metals are rarely used in pure form, even gold for jewellery is alloyed, e.g. with silver or nickel. Some well known base metals, like aluminium, magnesium and iron are only used practically in the form of alloys. Aluminium needs alloying elements, like Si, Cu, Zn, Fe, Mn or Mg, to compensate for the insufficient firmness, castability etc. of its pure form. Magnesium is alloyed to make it less reactive to oxygen in air and castable as well. Iron is by far still the most important metal for the human civilisation, but only applied as steel i.e. an alloy with carbon, and when alloyed with Ni and Cr it is called stainless steel. In this book the word "metal" covers both pure and alloyed metals.

There are countless fields of application where metals are combined with other metals, organic compounds or inorganic compounds. These combinations are found in the form of mechanical connections (by screws, rivets, by soldering or welding, or by means of adhesives) or coatings on metals (by painting or electroplating). The almost unlimited number of combinations between metals and other non-metallic components, their shapes, sizes, bulk densities, degree of contamination by every conceivable kind of dirt, etc., set the tone of the recycling business. Hence recycling, even strictly focussing on metals, has to deal with non-metallic material as a typical by-product of metal containing goods and articles. Due to the enormous variety of existing bonds between metals and non-metallic components, the process of metallic scrap preparation is technologically much more ambitious than any existing ore beneficiation process. The purpose of scrap preparation is to separate, by mechanical or physical (not chemical or thermal) means, as much non-metallic material as possible under the prerequisite of minimal metal losses. In the case of metal bearing ores, grinding is an essential step of mechanical separation, in which individual minerals can be distinguished and hence separated by various mechanical means, including flotation etc. Grinding in the form of crushing and shredding is also a key operation for metallic scrap preparation, there are, however, serious limitations to these unit operations. Crushing or shredding a piece of metal which is coated by paint or plastic foil, or connected with glass by chemical adhesive, will simply produce a smaller piece of that metal, which is still connected with non-metallics. This results in no separation effect and reflects one characteristic of recycling: Minimising particle size cannot always solve separation problems, and even if proven applicable needs careful design.

Metal recyclers therefore have to accept almost any shape, size and composition of products containing the metal to be regained, and the technology applied has to be able to deal with the fact that there are no limitations in feed specification, and hence no standardised basis for process design and plant layout. Moreover, in course of time the physical and chemical composition of metallic scrap changes, often suddenly and drastically. From one week to the next a car manufacturer can decide to change the material of a gear-box from aluminium to magnesium alloy; hair dryers, previously made from steel, are now fixed into plastic casings; bicycles frames previously built from steel may today be made from carbon fibre reinforced resins or titanium or other exotic material combinations. Recycling and its technologies have to cope with all these varieties, for which only statistical information exists. To make things even more complicated, there are only statistical indications available once the products have reached their end-of-life. An aluminium beverage can may be back at the scrap smelter after as soon as 2 weeks or at latest after half a year; copper wire installations in a building will become available for recycling between 20 or 70 years after they are built-in. Metal recyclers therefore have to accept almost any shape, size and composition of products containing the metal to be regained, and the technology applied has to be able to deal with the fact that there are no limitations in feed specification, and hence no standardised basis for process design and plant layout. Moreover, in course of time the physical and chemical composition of metallic scrap changes, often suddenly and drastically. From one week to the next a car manufacturer can decide to change the material of a gear-box from aluminium to magnesium alloy; hair dryers, previously made from steel, are now fixed into plastic casings; bicycles frames previously built from steel may today be made from carbon fibre reinforced resins or titanium or other exotic material combinations. Recycling and its technologies have to cope with all these varieties, for which only statistical information exists. To make things even more complicated, there are only statistical indications available once the products have reached their end-of-life. An aluminium beverage can may be back at the scrap smelter after as soon as 2 weeks or at latest after half a year; copper wire installations in a building will become available for recycling between 20 or 70 years after they are built-in. Recycling is fed by products designed and artificially built by human beings and not generated by nature.

This is contrary to ores, which have specific characteristics according to the physical and chemical conditions in the surroundings effective over millions of years. From the composition of a shredded piece from a dish washing machine of 1965 one can neither point to the composition of the next piece from a dish-washer, nor to any other piece derived from electronics articles. In the moment metallic products are scrapped - whether promptly as production waste or collected after its end-of-life - there is no chance to detect a common process which will generally lead to the composition and size of exactly this scrap. This is in contrast to mineralisation processes in nature, which result in distinguished ore concentrations. Once understood one may search for similar conditions from past experiences and exploit this knowledge to make accurate predictions.

Therefore, generally speaking, recycling metallurgy is based on the theory and technology of the primary metals production: hydrometallurgy and pyrometallurgy, but with its own special characteristics due to feeds having often very different characteristics than geological ores. Although there are many similarities between primary and secondary extraction of metals, recycling metallurgy has significant difference from the primary metallurgy in various aspects, therefore, the processing principles and theory of the recycling metallurgy have its special focus. Table A.2 gives an overview on both the similarities and differences between the two, however, the thermodynamic principles remain the same in both cases!

A.2.1 Properties of materials,‘metals and alloys (by example)

The essential properties of various types of raw materials for recycling have been described by Henstock [321]. Here the properties of the products from the recycling metallurgy will be briefly discussed, namely pure metals and alloys. Other types of products such as chemicals or compounds are beyond the scope of this book. Due to the complexity of the raw materials in physical and chemical aspects, it is very important to bear in mind what products need to be produced to fit into the market. This is particularly important compared to the primary metals production, which normally lead to pure metals as the products.

Catergories of Raw Materials

Recycling will provide the European industry with domestic raw material and relieve its dependency on foreign imports. However, recycling has its limits. In general, there is no process without loss, no process using primary ores or concentrates runs without losses. A copper smelter is satisfied when producing 950 to 960 kg copper/t of copper in feed. Recycling returns material after its use for further processing. Accordingly an aluminium scrap smelter loses easily 10 to 15% of its metallic feed by oxidation or entrainment in slag or drosses. Winning metals from primary and second generation material as well is inevitably associated

Table A.2: Comparison of primary and recycling metallurgy

	Primary metals production	**Recycling metallurgy**
Raw materials	Ores of oxides, sulphides	Metal and alloy scraps, slags, flue dusts, used chemicals, etc.
Products	Pure metals, or ferroalloys	Pure metals, but mostly alloys
Processing technology	*Raw materials preparation:* Ore upgrading (grinding, physical separation: magnetic separation, gravity separation, flotation), pelletising, sintering *Pyrometallurgy:* Reduction of oxide ores, roasting of sulphide and subsequent reduction, sulphide smelting, matte converting, fire-refining, molten sat electrolysis. *Hydrometallurgy:* Ore leaching (acid, alkaline, bacteria, atmospheric or pressurised), purification (cementation, precipitation, ion exchange, solvent extraction), electrowinning and electrorefining	*Raw materials preparation:* Dismantling, sorting, shredding, mechanical separation (magnetic, gravity, flotation, eddy current) *Pyrometallurgy:* Co-processing in primary smelting circuit, fuming, reduction smelting, scrap converting, fire refining, remelting and refining, etc. *Hydrometallurgy:* Leaching (acid, alkaline, ammonia) of metals or oxide impurities, separation (precipitation, ion-exchange, solvent extraction), electrowinning and electrorefining

with losses. Moreover any further fabrication of goods by all kinds of machining, produce further material losses. The steady stream of metal loss has to be compensated by primary material, i.e. a steady stream of ores and concentrates is still necessary, even if recycling runs at its optimum. There is no global figure available for assessing this flow of primary resources. First of all the metal demand is still increasing. This means that even if 100% of a metal is recycled, by the time it reappears on the market it will not be sufficient to supply the ever increasing demand.

Example A.3

Assuming that the demand of a certain metal increases steadily by 3%/year and that the average life-span of the goods produced from it is 12 years. If the recycling rate (collection rate multiplied by metallurgical recovery rate) is 100%, the metal recycled after the first 12 years is 100%, however, the demand increased in the meantime to 143%. Primary metal winning from ores has to help out with a production of 43%. At realistic recycling rates of 65% the classical primary raw materials sector of mining and smelting has to substitute 78% of the actual demand.

This example is extremely simple and far off the complex reality, nonetheless, it demonstrates that primary raw material winning is necessary as long as demand increases, irrespective of actual recycling rates. It is evident that due to its very specific application sectors each metal is characterized by a specific maximal attainable recycling rate (MARR), irrespective of the above mentioned time component or losses during processing. The application of copper for example happens to be in products like electrical equipment, brass and bronze, etc. After the end of its life the copper is still there, can be taken back to a smelter and reduced again into metallic copper. The fraction of copper converted into copper salts for various purposes, is less than 2%, this amount is small but still decisive. This fraction of copper will most likely never return to a smelter, it may be dissolved by rain water (e.g. $CuSO_4$ for agricultural purposes) and flushed down the rivers into the ocean, i.e. it is irretrievable. The MARR for copper is therefore about 98%. Magnesium is used in sectors where the metal is converted into chemical compounds from which the metal cannot be extracted again: Magnesium is an alloying element for aluminium alloys (e.g. in beer or soft drink cans) and disappears in the cycle of aluminium; magnesium is used for desulphurisation of steel, whereby it is converted into sulphides and discarded with the slags; magnesium is used for self-sacrificing anodes for ships or pipelines, oxidized thereby and lost in soil or sea water; magnesium is used for fire-works where it is literally blown up and dispersed in air; magnesium is used for the reduction of some other metals like titanium and zirconium and thereby oxidised and slagged; only magnesium used for die-casting is in principle available for recycling. As this sector absorbs presently about 30% of the magnesium production (yet with a rate of increase of about 13%/a) the specific MARR of magnesium is equivalent to that percentage, i.e. about 30%. These two examples illustrate the difficulty associated in answering the question: What will the quantitative contribution of primary material winning be in the future? Nonetheless, the systematic registration of the specific MARR will avoid unjustifiable hopes about the contribution of recycling for each of the metals.

Categories of residual material Prior to any statement about recycling procedures the confusing diversity of residual material needs to be structured (Table A.3). For this purpose the source of origin as well as the different properties of residual material can be used. The origin of any residual material is somebody who would like to get rid of something which has lost its pristine function (often only in comparison the up-dated equipment). It could be an out-dated cellular phone or old-fashioned bicycle, a broken chain saw, but also burrs of castings, turnings and chips from machining prefabricated goods, slag and dross from melting, spent catalyst from cars or petrochemistry, a TV set rejected at the factory because of quality deficits, cartridges from spent ammunition as well as cables from a demolished building or metal containing sludges from electroplating. It seems difficult to detect common features. A first category for differentiation is the number of utilisation cycles the material has undergone. The above mentioned examples are now used to check this. The cellular phone has obviously reached its end-of-life, as well as the bicycle, the broken chain saw, spent catalysts, cartridges from spent ammunition and cables from demolished buildings. They emerge after passing a full cycle from primary metal winning to scrapping. According to our previous definition these materials are second generation residual material or old, collected residual material. Burrs, turnings, chips, slags, dross, rejected TV sets and alike stem from the very beginning of the first industrial utilisation cycle; these material have not seen any customer and can therefore called first generation residual material or prompt, new residual material. In terms of metallic scrap, second generation residual material is called old or collected scrap, first generation material is named prompt, new or production scrap.

Table A.3: Categories of metalliferous material

	Categories according to number of passed utilisation cycles	
	In the first cycle	In the second or higher cycle
Origin	first generation material (FGM)	second generation material (SGM)
Natural Source	ores	
Use	prompt or new scrap examples: turnings, dross, slags, sawdust, rejects, billet residues etc.	collected or old scrap examples: end-of-life goods, old cars, old household wares

The difference between both the categories is mainly the temporal actuality of composition. Second generation residual material may stem from weeks, years or decades ago; that is why for a heap of scrap only one statement can be made: It contains material as old as anyone likes, i.e. there is no hint about composition at all. Prompt residual material, however, is just a few days or weeks old and reflects the composition of material presently in use - in many cases specifications of the material are available. The time difference between first and second generation residual material is at least 1 utilisation cycle, which for packaging goods could be months, for cars years, for material in buildings, ships or air planes decades.

Essential Properties of Residual Material Metal containing residual material, like the aforementioned examples, ontain considerable amounts of non-metallic components, which, at least for the sake of metal extraction, should be separated before the resulting metal concentrate - even if the metal concentrate is a polymetallic one - is further processed. In the case of dish-washing machines or cellular phones the non-metallic components could be separated after the machine is totally but orderly dismantled. Despite its impracticability due to the endless variety of different models, the sacrifice of time would be in the same order as that of its assembly, i.e. the recycling charges necessary to cover the cost would be exorbitant. Crushing or shredding such machines first of all delivers smaller particles. Depending on the kind of bonds between the various materials, particles will predominantly consist of relatively "clean" metal and "clean" non-metallics, or the particles will still be contaminated with foreign material. In the first case relatively simple separation techniques can immediately be applied to the mixture in order to separate metallic from non-metallic particles. As metals are strong electrical conductors compared with non-metallic components, separation will use these distinct differences of physical behaviour, resulting in a "clean" metal concentrate and minimal metal losses in the non-metallic fraction. In the second case further pre-treatment of the particles is necessary, before any metallurgical processes can even be considered, otherwise the metallurgical smelter would work as a waste incinerator, or a hydrometallurgical plant would be burdened by an extraordinary output of filter cake for disposal. Prior to any decision about further pre-treatment of still complex composite particles, the various properties of the residual material have to be evaluated regarding its effectiveness. Table A.4 summarises chemical and physical properties of material, which are useful at different steps of recycling. Here M refers to properties which motivate recycling efforts.

Table A.4: Material properties used in various phases of recycling metalliferous residual material

	Units	Pre-treatment and Conditioning	Concentration of Valuable Components	Processing and Winning
Content of Valuables	wt. %	M	M	M
Scarcity, Shortage	ton	M	M	M
Heat Value	MJ/kg	X		X
Density	kg/m^3		X	
Impurity Content	wt. %	X		
Particle Size	m		X	
Melting Temp.	°C			X
Conductivity	m·S		X	
Viscosity	m·Pas		X	X
Strength	N			
Surface Tension	N	X	X	X

Metals and alloys

Pure metals have many superior properties over other types of engineering materials such as plastics and wood due to its strength, durability, and other properties to be shown below. However, only a few metals are used in practice as pure metals. When a metal is mixed with another metal or a few other metals, an alloy is formed. Often the alloys exhibit superior properties of hardness, strength, toughness etc. over the individual pure metals. It is particularly important for recycling metallurgy to understand metal alloys and their properties, since most of the products from the metal recycling are in alloy form. To produce appropriate alloy composition with required properties is critical for recycling metallurgists.

In general, an alloy exhibits metallic properties, with a change in properties compared to the original metals. In industry, a couple of thousands of alloys are available for practice use. But all the alloys basically fall into 4 types, which are summarised below [395]:

- **The solid solution alloy system (Type I alloy):** The two metals are completely soluble with each other, with infinite solubility. Example: Cu-Ni alloy.
- **Eutectic alloys (Type II alloy):** two components insoluble in solid state: Both majority (parent) and minority alloying elements maintain their individual identities.

The alloy has a composite structure and mixed properties of each elements. Example:

- **Partial solubility in solid state (Type III alloys)**: The parent is called solvent, and the alloying element is called solute.
  - Substitutional: solute atoms replace the solvent atoms.
  - Interstices: solute atoms are smaller to fit into the spaces between the solvent atoms
- **Intermetallic compounds (Type IV alloys)**: the metallic elements combine to form a compound in definite proportion. Intermetallic compounds are principal hardeners and are present in steel or aluminium alloys.

Durability

Metal products may loose their functionality at the end of the useful life, and become scraps. Different from other materials like plastics, metals maintain their basic properties with little of no degradation after use and reuse. This special characteristics of metals makes the metals directly recyclable, and links to another important property of metals: recyclability.

Recyclability

Though metals and their alloys could be recycled to gain their new service life, the effort to be made to recycle the metals depends on the quality of the scraps, and this is also related to the original form of the product. It is evident that in general alloys have relatively lower recyclability than pure metals after their end of life, which means that pure metals bear higher recyclability than alloys. Recyclability of metal scraps are discussed in more detail in Parts III and IV. The following discussion will go to the conventional description of physical and mechanical properties of metals and alloys. Only a short description will be given, and more details could be found in most of the metals reference books.

Table A.5: Properties of metals and alloys

Thermophysical properties	Density Heat capacity Thermoconductivity Thermal expansion coefficient
Mechanical properties	Corrosion resistance Abrasion resistance Fatigue resistance Creep resistance Ductility Castability Formability Hardness Strength Toughness
Chemical properties	Catalytic properties
Magnetic properties	Electrical conductivity Magnetic permeability

A.2.2 Metallurgical thermodynamics

It is clear that metallurgical processes for recycling (from chemical reaction point of view) is governed by thermodynamics which gives the potential and limit of a chemical process (e.g. purification and phase separation), and reaction kinetics which indicates the rate to reach a equilibrium thermodynamic state. Process metallurgists are very familiar with both types of knowledge, and they are considered to be equally importance. In the following text, a brief summary is given to both metallurgical thermodynamics and reaction kinetics, illustrated with examples in recycling metallurgy. As is also known that molten slags and fluxes, and alloys are all important parts in the metals recycling, the thermodynamics of those systems will be discussed separately below under: slags, fluxes and alloys. The purpose of introducing thermodynamics in the current context is not meant to give extensive coverage of the basic theory of the thermodynamics, rather a summarizing information is supplied. It is also assumed that the readers of this book has already the basic knowledge of thermodynamics and specifically the theory related to process metallurgy. Here the emphasis is laid on its relevance to the recycling metallurgy: processing of secondary metals. For a complete theory of metallurgical thermodynamics, please refer to the monographs by Rao [396], Rosenqvist [397], Gaskell [398], Devereux [399], and Upadhyaya [400].

Metallurgical thermodynamics normally covers the following topics:

- **Thermochemistry**: The First Law of Thermodynamics, which tells about the law of energy conservation. The basic concepts of enthalpy, enthalpy changes involved with a chemical reaction, calorimetry, and industrial energy balances are introduced.
- **Chemical equilibrium**: The Second Law of Thermodynamics, which tells about to which extent a chemical reaction could reach. The basic concepts of entropy, Gibbs free energy, and free energy changes of chemical reactions are introduced.
- **Melts and solutions**: molten metals and alloys, molten slags and molten salts are important parts of metallurgy, and are discussed. Activity, thermodynamics of solutions and phase diagrams are important knowledge for recycling metallurgy. This will be handled separately in this chapter.

In order to avoid exhaustive repeating the basics of thermodynamic theory, here only the essential thermodynamic laws will be addressed, and the possible applications in recycling metallurgy will be exemplified when it is possible.

Thermochemistry

The first law of thermodynamics It tells about the overall energy conservation of a system. The system could be a reactor such as smelting or melting furnaces, or a control volume of a reactor. The same principle applies. In general, it could be stated for a general system that:

- The total energy change of a system from state 1 to state 2, is equal to the heat added to it, minus the useful work performed by the system.

This way of statement is useful for any attempt to make an energy balance, e.g. for a reactor or furnace. If we look at the system from a control volume point of view (the control volume could be a macroscopic or a microscopic volume), it could also be stated that:

- The amount of the thermal energy and mechanical energy that enters a control volume, plus the amount of the thermal and mechanical energy that is generated within the

> control volume, minus the thermal and mechanical energy that leaves the control volume, must equal the increase in the amount of the energy stored in the control volume.

This way of statement is useful for heat transfer analysis of a reactor system.

Enthalpy and enthalpy changes in chemical reactions Enthalpy is the basic building block for any kind of energy balance and thermal analysis. The enthalpy is defined as the sum of the internal energy (U) and the product of pressure (P) and system volume (V), i.e.

$$H \equiv U + PV \tag{A.35}$$

At constant pressure and if no works other than reversible volume work is done, $dH = \delta q$, and the change in enthalpy equal to the heat absorbed (q) of the system. That is,

$$(\Delta H)_P = H_2 - H_1 = q \tag{A.36}$$

Since most of the chemical and metallurgical processes are operated at constant pressure, it is very convenient to use the enthalpy function to make energy calculations and thermodynamic analysis. In the same way, the internal energy change of a system equal the heat absorbed at a constant volume.

$$(\Delta U)_V = U_2 - U_1 = q \tag{A.37}$$

However, very few processes are carried out at constant volumes. Since the absolute values of U and H are unknown, it is often in practice to use the change of enthalpy or sometimes internal energy. To calculate the change of enthalpy of internal energy, heat capacity or specific heat is required. In relation to U and H, there are two types of heat capacity:

1. heat capacity at constant volume C_V
2. heat capacity at constant pressure C_P

They are defined as the partial derivative of U or U with respect of temperature T, as follows:

$$C_V = \left(\frac{\delta U}{\delta T}\right)_V \quad \text{and} \tag{A.38}$$

$$C_P = \left(\frac{\delta U}{\delta T}\right)_P \tag{A.39}$$

However, all the C_P or C_V values are obtained from experiments, and could not be calculated thermodynamically or theoretically. With this definition, change of H could be calculated as follows, and the change of U could be calculated in the same way with C_V:

$$\Delta H = H_{T_2} - H_{T_1} = \int_{T_1}^{T_2} C_P dT \tag{A.40}$$

Or at standard state,

$$\Delta H = H^\circ_{T_2} - H^\circ_{T_1} = \int_{T_1}^{T_2} C_P dT - \sum \Delta H_{T_{ref}} \tag{A.41}$$

It is very useful to have the relationship between specific heat C_P and temperature T, which could be used to calculate the enthalpy change of e.g. a reaction. Often within a certain temperature range molar specific heat is expressed in the following form:

$$C_P = a + bT + cT^2 + ... + eT^{\;2} \qquad (A.42)$$

As mentioned above, the values or the temperature dependency of Cp are obtained through experiments, and could be found in many thermodynamic handbooks, e.g. "Metallurgical Thermochemistry" by Kubaschewski and Alcock [401]. As metallurgists we are also concerned with the enthalpy changes for chemical reactions. The enthalpy change for a chemical reaction (isothermal enthalpy, ΔH_T) is defined as the difference between the total enthalpy of the reaction products and the total enthalpy of the reactants at a given temperature T:

$$\Delta H_T = \left(\sum \delta H_{T,i}\right)_{Products} - \left(\sum \delta H_{T,j}\right)_{Reactants} \qquad (A.43)$$

If the reaction takes place at a constant pressure and without other work, the isothermal enthalpy equals the amount of heat absorbed from or released to the surroundings. If both the reactants and the products are in standard state (that is subject to preferences), the enthalpy of reaction is referred to as ΔH_T^o. For a compound formed from individual elements, the enthalpy change is knows as the heat of formation. Often the standard state is chosen at a temperature of 25C (298 K) and a pressure of 1 atmosphere (1 bar), and then the standard enthalpy of a reaction is denoted as ΔH_{298}^o and are available in most of the thermodynamic data books. As a convention, the standard heat of formation is assumed to zero for the element, including compounds from the same element like oxygen (O_2).

From metallurgical point of view, the following concepts or functions are very important: **heat of reaction, heat of formation, heat of combustion**, and **heat of solution** [400]. They are therefore discussed briefly as below.

Heat of Reaction, Formation, Combustion, and Solution **Heat of formation** per mol of a compound is the heat released or absorbed when one mol of the compound is formed from its constituent elements. At the standard state, it is called **Standard Heat of Formation.** It is the enthalpy change of a chemical reaction at standard state when individual elements react to form a compound, ΔH_{298}^o, as is described earlier. This is very important when you attempt to make any heat balance for a reacting system. For example, when aluminium metal is oxidised when it is being melted in a secondary aluminium smelting furnace, a lot of heat is being released. The heat release may contributes significantly to the overall energy balance. However, you must know how much aluminium is being oxidized and how much heat is being generated. This could be illustrated in the following example.

Example A.4

Estimate the heat release of aluminium oxidation in a secondary smelting furnace

Oxidation of aluminium metal is an irreversible loss of metal, and should be minimized in the smelting and refining operation. However, oxidation of aluminium metal is a highly exothermic reaction. Please estimate the total heat released when 1 kg Al *metal is being oxidized at 500° C in a remelting furnace.*

Answer: *The oxidation reaction is as follows:*

$$2\text{Al(s)} + \frac{3}{2}\text{O}_2\text{(g)} = \text{Al}_2\text{O}_3\text{(s)} \qquad (A.44)$$

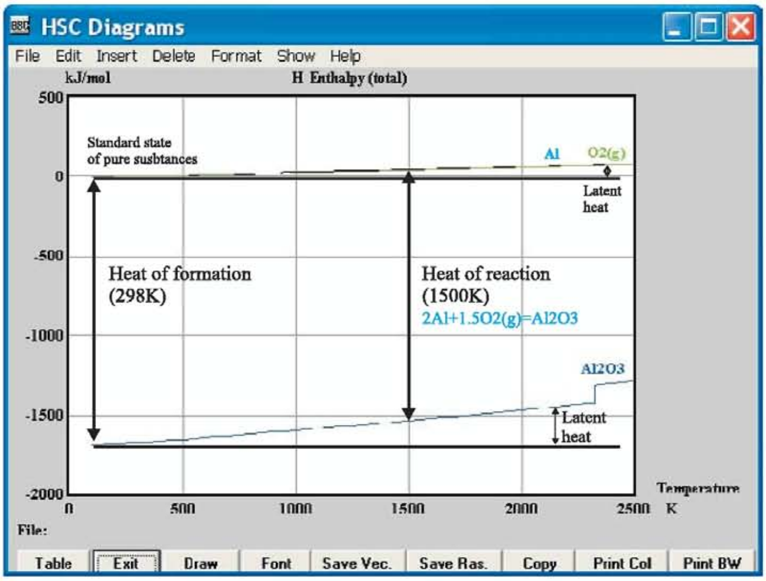


Figure A.11: Definition of standard state, heat of formation, reaction enthalpy, definition of latent heat: for the oxidation of aluminium metal to for Al_2O_3

At constant pressure, the total heat release equals the enthalpy change of the oxidation reaction of Al *metal at 500° C (773 K). This could be easily calculated from the standard heat of formation of* $Al_2O_3(s)$, ΔH°_{298}, *plus the enthalpy difference between the product* (Al_2O_3) *and the reactants* (Al *and* O_2) *from 298 K to 773K, i.e.* ΔH^{773}_{298}.

$$q_{773} = \Delta H_{773} = \Delta H^\circ_{298} + \Delta H^{773}_{298} \tag{A.45}$$

The standard heat of formation is the heat release at standard conditions (298K and 1 atm), and this is not the same if the reaction takes place at different temperatures. For example, from "Metallurgical Thermochemistry" by Kubaschewski and Alcock [401], the standard heat of formation of $Al_2O_3(s)$ *is -400.0± 1.5 kcal/mol, that is -1675 kJ/mol* Al_2O_3. *The complex part is to calculate the second term on the right hand side of the above equation,* ΔH^{773}_{298} *(is also called the latent heat). The enthalpy change can be then calculated according to the* C_P *functions of each substance as follows (see also Figure A.11):*

$$\begin{aligned} \Delta H^{773}_{298} &= \left(\Delta H^{773}_{298}\right)_{product} - \left(\Delta H^{773}_{298}\right)_{reactants} = \left(\Delta H^{773}_{298}\right)_{Al_2O_3} \\ &- \left(\Delta H^{773}_{298}\right)_{Al,O_2} = \int_{298}^{773} \left(C_{P,Al_2O_3}\right) dT \\ &- \int_{298}^{773} \left(2C_{P,Al} + \frac{3}{2} C_{P,O_2}\right) dT = \int_{298}^{773} C_P dT \end{aligned} \tag{A.46}$$

From Kubaschewski and Alcock [401], the temperature dependent specific heat ($J/K \cdot mol$) *for all three substances are:*

$$C_{P,Al(s)} = 20.65 + 12.37 \cdot 10^{-3}T \tag{A.47}$$

$$C_{P,O_2(g)} = 29.93 + 4.18 \cdot 10^{-3}T - 1.67 \cdot 10^{-5}T^{-2} \tag{A.48}$$

$$C_{P,Al_2O_2(s)} = 106.51 + 17.77 \cdot 10^{-3}T - 28.51 \cdot 10^{-5}T^{-2} \tag{A.49}$$

Therefore, the C_P difference could be calculated as:

$$\begin{aligned} \Delta C_P &= C_{P,Al_2O_3} - 2C_{P,Al} - \frac{3}{2}C_{P,O_2} \\ &= 20.32 - 13.24 \cdot 10^{-3}T - 28.51 \cdot 10^{-5}T^{-2} \end{aligned} \tag{A.50}$$

The integration over the temperature difference from the standard state (298K) results in:

$$\begin{aligned} \Delta H_{298}^{773} &= \int_{298}^{773} C_P dT \\ &= \int_{298}^{773} \left(20.32 - 13.24 \cdot 10^{-3}T - 28.51 \cdot 10^{-5}T^{-2}\right) dT \\ &= 920.8 \left(\frac{J}{K \cdot mol}\right) \end{aligned} \tag{A.51}$$

The total heat release is then the sum of the two parts of the enthalpy change: the standard and the part due to temperature increment:

$$\begin{aligned} q_{773} &= \Delta H_{298}^{\circ} + \Delta H_{298}^{773} = -1,675 + 0.921 \\ &= -1.674 \left(\frac{kJ}{mol\ Al_2O_3}\right) \end{aligned} \tag{A.52}$$

This could be simply converted to the value based on 1.0 kg aluminium metal, according to the stoichiometry of reaction (Eq. A.44). To form 1 mol of $\mathrm{Al_2O_3}$*, requires 2 mol of aluminium metal, i.e. 54 g* Al*. Therefore, to oxidize 1000 g* Al *metal,* $\frac{-1674 \times 1000}{54} = 31,001$ *kJ (31MJ) heat is released. It could be seen that the oxidation of aluminium metal is a highly exothermic reaction, its standard heat of reaction, 31 MJ/kg* Al*, is close to many hydrocarbons* ($\mathrm{CH_4}$*: 50 MJ/kg low heating value). Figure A.12 illustrates the temperature dependency of the heat release of the aluminium oxidation, according to the following correlation (from temperature dependent C_P functions).*

$$\begin{aligned} q_T &= -1689196 + 20.32T - 6.62 \cdot 10^{-3}T^2 \\ &+ 26.01 \cdot 10^5 T^{-1} \left(\frac{J}{mol\ \mathrm{Al_2O_3}}\right) \end{aligned} \tag{A.53}$$

Remarks : It is now clear that the heat release at 500°C is only slightly lower than the room temperature value. The temperature dependency of the heat release is determined by the temperature dependence of the C_P values of the reactants and products. Based on the C_P functions as temperature, the heat release at any temperature above room temperature

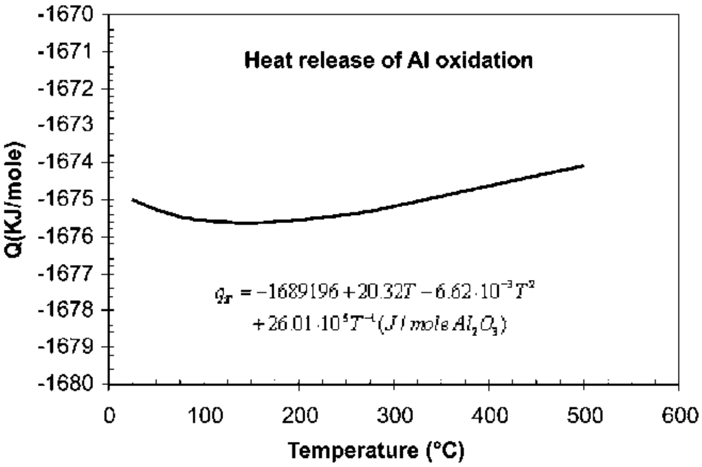


Figure A.12: Heat release during oxidation of aluminium metal to for Al_2O_3

could be easily calculated, and be plotted. Nowadays, this type of calculations could be easily done with thermodynamic software, such as HSC Chemistry 5.1 [402]. With mass and energy balance module, the materials and energy balance could be flexibly conducted for a reaction. When carrying out the energy calculations, one should keep in mind that if a material or substance experiences a phase change or phase transformation at the temperature range concerned, the corresponding enthalpy change should be added. Many metals and the compounds have different structures at different temperature ranges, e.g. metallic iron (Fe) in α, β and γ structure.

Heat of Combustion of a substance is the enthalpy change when one mol of the substance is completely burnt or oxidized in oxygen. The data for both **Heat of Formation** for most of the compounds and **Heat of Combustion** for most fuels are available in common thermodynamic data book or software such as Handbook of Chemistry and Physics [403], or calculated from HSC Chemistry, where the basic Cp values and temperature dependent formulas are available. **Heat of Combustion** is an important data for pyrometallurgical furnace design and operation. Based on the heat of combustion of a certain fuel, it is possible to calculate the maximum reaction temperature for an adiabatic system (T_m): **Flame Temperature**. In general, the combustion of a fuel could be represented as follows:

$$[\text{fuel} + \text{oxidant}]_{298,K} \xrightarrow{q} [\text{Combustion products}]_{T_m} \tag{A.54}$$

The heat of combustion from the fuel (q) at standard state is used to exclusively heat up the combustion products to its flame temperature T_m. Then the flame temperature could be easily calculated as follows:

$$q = \int_{298}^{T_m} \sum C_{P,products} dT \tag{A.55}$$

Since C_P is temperature dependent, and T_m has to be determined after the integration. If the oxidant is air or with other inert components, they should be included in the products which requires to be heated up to the same flame temperature. In the broader sense, if the system is not adiabatic, e.g. with heat loss, the maximum flame temperature under non-adiabatic condition could be in the same way calculated, keeping in mind that heat loss q_{loss} must be subtracted from in Equation A.55, i.e. a net heat is needed q_{net} in Equation A.55.

Example A.5

Calculation of adiabatic flame temperature of a rotary aluminium refining furnace.

In secondary aluminium remelting and refining processes, rotary furnaces are often used to melt the scrap and refine the metal. The energy required to heat up and melt the scrap and sometimes salt comes from the combustion of natural gas with pure oxygen. The composition of the natural gas is roughly 90% CH^4 *(including a few percent of other combustibles) and 10%* N_2.

***Answer**: Assuming that all the fuel is in* CH_4 *form and the heat of combustion (low value - i.e. water is in vapour format) is about 50.16 MJ/kg or 802.56 KJ/mol, or 35.94 MJ/Nm*^{3} CH_4. *The combustion reaction of the above system can be written as follows:*

$$[CH_4 + 2O_2 + 0.11N_2]_{298,K} \xrightarrow[802.56kJ]{q} [CO_2 + 2H_2O + 0.11N_2]_{T_m} \tag{A.56}$$

If no excess oxygen is supplied, under adiabatic conditions the maximum flame temperature can be calculated according to Equation A.55 as follows:

$$\begin{aligned} q &= \int_{298}^{T_m} \sum C_{P,products} dT \\ &= \int_{298}^{T_m} (C_{P,CO_2} + 2C_{P,H_2O} - 0.11C_{P,N_2})\, dT \end{aligned} \tag{A.57}$$

The following C_P functions could be found from "Metallurgical Thermochemistry" by Kubaschewski and Alcock [401] converting SI unit:

$$C_{P,CO_2} = 44.10 + 9.03 \cdot 10^{-3}T - 8.53 \cdot 10^{-5}T^{-2} \tag{A.58}$$

$$C_{P,H_2O} = 29.97 + 10.7 \cdot 10^{-3}T - 0.33 \cdot 10^{-5}T^{-2} \tag{A.59}$$

$$C_{P,N_2} = 27.84 + 4.26 \cdot 10^{-3}T \left(\frac{J}{K \cdot mol}\right) \tag{A.60}$$

Inserting all the $C_P$functions, and integrating, we can get:

$$\begin{aligned} q &= \int_{298}^{T_m} (93.10 + 30.90 \cdot 10^{-3}T - 9.19 \cdot 10^{5}T^{-2})\, dT \\ &= \left|93.10T + 15.15 \cdot 10^{-3}T^2 + 9.19 \cdot 10^{5}T^{-1}\right|_{298}^{T_m} \\ &= -32199.71 + 93.10T_m + 15.45 \cdot 10^{-3}T_m^2 + 9.19 \cdot 10^{5}T_m^{-1} \end{aligned} \tag{A.61}$$

Replacing q with 802.560 J (please using positive value here), we get the following T_m function. But noting that it involves with T-1, an analytical solution is not directly available.

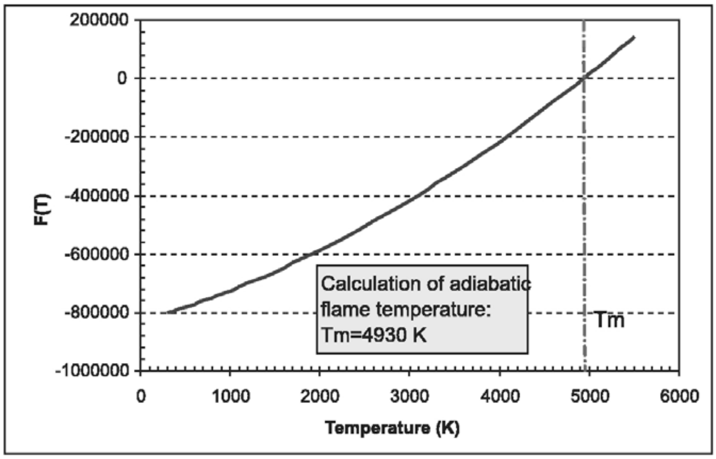


Figure A.13: Adiabatic flame temperature calculation for Example A.5

However, we could use graphical approximation by drawing the function F(T), and get the T_m *when F(T)=0.*

$$F(T) = -834759 + 93.10T + 15.45 \cdot 10^{-3}T^2 + 9.19 \cdot 10^5 T^{-1} \tag{A.62}$$

Using Excel by plotting F(T) at different given temperatures, one can get roughly the value when the curve crosses horizontal T axis (Figure A.13), i.e. the adiabatic flame temperature T_m*. Thus, a maximum flame temperature in this system is about 4930 K or 4657° C.*

Hess' Law Hess' law states that the heat content change in a chemical reaction is the same whether it takes place in one or several stages, provided the temperature and either pressure or volume remains constant. This allows the heat of formation or reaction can be deduced with known data from other relevant reactions. For instance, we know now the standard enthalpy of reaction of the following reactions:

$$\mathrm{W_{(s)} + O_{2(g)} \rightarrow WO_{2(s)}} \qquad \Delta \mathrm{H}^\circ_{298,a} = -560.66\mathrm{kJ} \tag{A.63}$$

$$\mathrm{3WO_{2(s)} + O_{2(g)} \rightarrow W_3O_{8(s)}} \qquad \Delta \mathrm{H}^\circ_{298,b} = -550.20\mathrm{kJ} \tag{A.64}$$

$$\mathrm{W_3O_{8(s)} + 0.5O_{2(g)} \rightarrow 3WO_{3(s)}} \qquad \Delta \mathrm{H}^\circ_{298,c} = -278.24\mathrm{kJ} \tag{A.65}$$

We want to know the standard heat of formation of WO_3 as represented in the following equation A.66.

$$\mathrm{W_{(s)} + 1.5O_{2(g)} \rightarrow WO_{3(s)}} \qquad \Delta \mathrm{H}^\circ_{298,d} \tag{A.66}$$

We could use the know data from above reactions A.63 - A.63 to derive the reaction heat of reaction A.66, by doing: (a)+1/3(b)+1/3(c)=(d). The heat of formation of reaction (A.66) is then simply equal to:

$$\Delta H^\circ_{298,d} = \Delta H^\circ_{298,a} + \frac{1}{3}\Delta H^\circ_{298,b} + \frac{1}{3}\Delta H^\circ_{298,c} \tag{A.67}$$

$$= 836.81 \ \frac{kJ}{mol \ \mathrm{WO}_{3(s)}} \tag{A.68}$$

For more details, please refer to the book by Upadhyaya and Dube [400].

Heat of solution "Heat of solution" refers to the enthalpy change when one substance dissolves in another (the solvent), thus forming a solution. The heat of solution depends on the concentration of the solution. This may takes place when an alloying element dissolves into a molten metal to form an alloy. However the heat of solution depends on both temperature and the concentration of the solute in the solvent. Some data are available for various binary alloy systems, e.g. "Metallurgical Thermochemistry" by Kubaschewski and Alcock [401]. Heat of solution is further subdivided into **Integral** and **Partial** heat of solution, which will be described later in Section A.2.2. For example, the Al-Cu binary alloy system, the integral heat of solution at 1373 K (1100°C) at different mol fractions of Cu is as follows:

Table A.6: Examples of solution heat of a binary alloy system: Al-Cu alloy

X_{Cu}	0.0	0.1	0.3	0.5	0.7	0.9
Δ H(Cal/g-atom)	0	-459	-1445	-2163	-1980	-800
Δ H_{Cu}	-4225	-4850	-4675	-3270	-680	-65

Industrial enthalpy balances Having now sufficient knowledge of metallurgical thermochemistry, it is easy to make an energy balance for an industrial chemical process. For detailed information, please refer to "Principles of Extractive Metallurgy" by Rosenqvist [397].

To make a complete energy balance of a metallurgical process, the following aspects need to be considered:

1. Physical heat of all raw materials into the reactor (Input),
2. Physical heat of all products leaving out of the reactor (Output),
3. Standard heat of chemical reactions, including heat of solution etc. if any,
4. Heat loss of the reactor (Part of the output).

For items 1 and 2, it is straightforward. Normally we choose the standard state at 298 K and 1atm pressure. Then all the thermodynamic data required (C_P and normally) are available and easy to find. The heat of chemical reactions (at the reference temperature and pressure, i.e. the standard state) can be calculated based on the individual compounds or elements involved as is discussed earlier in this section. Heat of a chemical reaction may be positive (absorbing heat) as a heat sink or negative (releasing heat) as a heat source. Sometimes, people try to group all the positive items as "input", and all the negative items as "output". In this book, all the input and output are just physical sensible heat relative to the reference temperature (e.g. 25°C or 298 K). Then the energy balance (surplus or deficit) will be:

$$\begin{aligned}\text{Heat balance} &= \sum(Output) - \sum(Input) \\ &+ \text{Standard heat of reaction}\end{aligned} \tag{A.69}$$

The unknown to be determined could be:

- Heat surplus or deficit, if the temperature of the system is predefined. In this case, either a heat loss could be calculated if there is surplus, or the extra work/energy from the surroundings needs to be supplied such as electrical heating if there is a deficit.
- The final temperature of the system, if the heat surplus or deficit is predefined or known. On the other hand, the reference temperature could also be arbitrary. This could be 25°C for most of the cases, or another temperature e.g. the temperature of a reactant, or product. However, the final result of the heat surplus or deficit remains the same, although other terms may differ significantly from the values at 25°C.

When an alloy is formed from individual metals or a molten slag is formed from individual compound, the heat of solution of an alloy or slag system need to be included. However, the heat of solution for most of the slag systems is not easy to find.

Example A.6 illustrates how to make an energy balance for a copper-making PS-converter which converts Cu_2S to metallic copper (the second phase of copper converting) [397]. It will be seen that there will be an energy surplus, which should be removed. In copper making, it is sometimes to add copper scraps directly to the PS-converter to recycle the copper and utilise the extra heat generated from the oxidation of cuprous sulphide. First, we follow the above-mentioned 4 steps, to calculate each item, and determine the heat surplus which is available partially to remelt copper scrap and partially to the environment. Then we perform the calculation with HSC Chemistry and compare the results.

Example A.6

Heat balance for a copper making PS-converter. PS-converter is used to oxidize copper matte (Cu_2S+FeS) *to metallic copper. The process is highly exothermic. In order to utilize the extra thermal energy, scrap copper Cu-bearing revert materials, and sometimes copper concentrates are charged directly into the converter, to maximize the energy utilization efficiency. However, it is important that the addition of the cooling charges do not affect the converting temperature, that is overcooling should be avoided. Therefore, an energy balance is essential to guide the extra solid charging operation.*

Copper converting takes place in two distinct stages:

1. ***The slag-forming stage:*** *oxidation of* FeS *and the formed* FeO *slagging with* SiO_2*. This is highly exothermic, and the standard reaction enthalpy is -462.41 kJ/mol* FeS*, (if both* FeS *and* FeO *are in solid state) and at 1200°C the reaction enthalpy is -502.79 kJ/mol* FeS *(if* FeS *in liquid state and* FeO *in solid state), calculated with HSC Chemistry 5.1 [402].*

$$FeS_{(l)} + 1.5O_{2(g)} \rightarrow FeO_{(l)} - SO_{2(g)} \tag{A.70}$$

In addition, slag formation heat could also be estimated, by assuming FeO *reaction with* SiO_2 *to form fayalite* $2FeO \cdot SiO_2$*. the standard enthalpy of the slag formation is about -26.1 kJ/mol* $2FeO \cdot SiO_2$ (γ) *at 25°C, and -32.95 kJ/mol* $2FeO \cdot SiO_2$ (γ) *at 1200°C.*

However, the fayalite formed will be dissolved in the slag and form a molten melt with other components. A small amount of heat of solution will be resulted, and this part is still difficult to characterise for slag systems.

$$2FeO_{(s)} + SiO_{2(g)} \rightarrow 2FeO \cdot SiO_{2(s)} \qquad (A.71)$$

2. ***The coppermaking stage**: the oxidation of cuprous oxide to metallic copper. This is also exothermic, but less than the slag-forming stage. The standard reaction enthalpy at 25° C is -217.32 kJ/mol* Cu_2S *(if both* Cu_2S *and* Cu *are in solid state), and at 1200° C is -218.66 kJ/mol* Cu_2S *(if both* Cu_2S *and* Cu *are in liquid state), calculated with HSC Chemistry 5.1 [402].*

$$Cu_2S_{(l)} + O_{2(g)} \rightarrow 2Cu_{(l)} + S_{2(g)} \qquad (A.72)$$

For a copper matte with about 65 wt.% of Cu*, the mol ratio of* Cu_2S/FeS *in the matte is close to 2. Now let's make a rigorous energy balance for both stages of the copper converting. The starting point is: 3 mol of copper matte consisting of 2 mol of* CuS *and 1 mol of* FeS*, is oxidised in two steps with stoichiometric air (no excess air). The matte comes in at about 1200° C, the copper and slag as well as the off-gas produced are also at 1200° C. The incoming blowing air is at 25° C. What is the heat surplus or deficit?*

Approach I: Using HSC Chemistry

1. ***Slag forming stage***

   Overall reaction

$$\begin{aligned} &FeS_{(l)}(1473K) + 0.5SiO_{2(s)}(298K) + [1.5O_{2(g)} + 5.64N_{2(g)}](298K) \rightarrow \\ &[0.5(2FeO \cdot SiO_2)_{(s)} + SO_{2(g)} + 5.64N_{2(g)}](1473) \end{aligned} \qquad (A.73)$$

   Enthalpy = -207.9 kJ/mol FeS

2. ***Coppermaking stage***

   Overall reaction:

$$\begin{aligned} &Cu_2S_{(l)}(1473K) + [O_{2(g)} + 3.76N_{2(g)}](298K) \rightarrow \\ &[2Cu_{(l)} + SO_{2(g)} + 3.76N_{2(g)}](1473K) \end{aligned} \qquad (A.74)$$

   Enthalpy = -39.1 kJ/mol Cu_2S

This calculation is quite similar to the step-by-step calculation by Rosenqvist [397]. His calculation for the coppermaking stage has a slightly different temperature: Cu_2S *at 1300° C, and all the products are at 1250° C. The heat surplus is -34.3 kJ/ mol* Cu_2S*, which is -34.93 kJ/ mol* Cu_2S*, with HSC. Therefore, the total energy release from both stages are: -286.1 kJ/ 3 mol* Cu *matte with the mol ratio of* Cu_2S/FeS *in the matte of 2. Thus for 1 mol matte of the above composition, the total heat release is -95.4 kJ, in which -31.8 kJ in slag-forming stage and -63.6 kJ in coppermaking stage. The copper matte with above molar composition contains 21.6 wt.%* FeS *and 78.4 wt.%* Cu_2S*, and thus for 1.0 kg matte (4.93 mol* Cu_2S *and 2.46 mol* FeS*) the available heat release could be calculated as -509.2 kJ from* FeS *and -192.8 kJ from* Cu_2S*. Now take a typical 200 ton matte/cycle PS-converter, and see how much copper scrap could be charged to the converter. Using the above assumptions and calculation result, the* *following table gives a good overview on total excess heat available in both stages. and the maximal allowed scrap charge as coolant.*

Melting 1 kg Cu *scrap (assuming pure copper) from 25° C to 1200° C, the enthalpy required could be calculated as follows in three steps:*

1. *heating up solid* Cu *from room temperature(25° C) to its melting point (1083° C)*
2. *melting at 1083° C*
3. *heating up of liquid* Cu *from 1083° C to 1200° C.*

With HSC Chemistry, it is straight forward in "energy and materials balance module", and the total heat needed is 0.73 MJ/kg.

Table A.7: General heat balance for a copper PS-converter

Item	Slag-forming stage	Cu-making stage
Available heat per mol (FeS or Cu_2S)	-207.9 kJ	-39.1 kJ
Available heat per kg matte	-509.2 kJ	-192.8 kJ
For 200 tons matte per cycle	-101,840 MJ	-38,560 MJ
Melting scrap: 25°C - 1200°C Unit consumption: 0.73 MJ/kg	139.5 ton Cu	52.8 ton Cu

In practice, due to heat loss of the converter and extra melting heat of impurities in the scrap and revert, and not overcooling the melt, up to 30% of blister copper product comes from the copper metal charging [404].

Approach II: Step-by-step calculation *Here we choose only the coppermaking stage as an example to illustrate the procedures. Similar to Rosenvist [397], the following reaction describes the case, at slightly different temperatures from the case in Rosenqvist:*

$$
\begin{aligned}
&Cu_2S_{(l)}(1473K) + [O_{2(g)} + 3.76N_{2(g)}](298K) \rightarrow \\
&[2Cu_{(l)} + SO_{2(g)} + 3.76N_{2(g)}](1473K)
\end{aligned}
\tag{A.75}
$$

We also choose 298 K as the reference temperature which will not influence the heat balance (surplus or deficit). We use "Raw materials" and "Products" to group all the items. With the know C_P functions of each individual substances, the Table A.8 shows the result.

The resultant figure of the total heat surplus (-38.32 kJ/mol Cu_2S*) is slightly different from the calculated value by using HSC-Chemistry shown earlier (-39.10 kJ), and is not very much different from the result from Rosenqvist [397] which has slightly different temperatures.*

Data reconciliation Mass and energy balances of reactors and plants based on measured process data often do not close. The usual reason is inaccuracy of the measurements as a result of the sampling, measurement, time and analysis errors. Data reconciliation is a technique that adjusts the process data such as flow rates and analyses to reduce and possibly eliminate discrepancies in the mass and energy balance. The adjusted data should give a more consistent representation of the actual process, which then forms the basis for any subsequent modelling activities such as thermodynamic modelling, kinetic modelling, computational fluid

Table A.8: General heat balance for a copper PS-converter

Raw materials (Input, mol)		
$Cu_2S_{(l)}$	ΔH_{298}^{1473}	116.75
O_2+3.76N_2	ΔH_{298}^{298}	0
Sub-total (kJ)		116.75
Products (Output, mol)		
$2Cu_{(l)}$	ΔH_{298}^{1473}	93.06
$SO_{2(g)}$	ΔH_{298}^{1473}	61.80
3.76 $N_{2(g)}$	ΔH_{298}^{1473}	140.89
Sub-total (kJ)		295.75
Standard heat of reaction		
$Cu_2S_{(s)} + O_{2(g)} \xrightarrow{298K} 2Cu_{(s)} + SO_{2(g)}$	ΔH_{298}^{o}	-217.32
Heat balance = $\sum$output - $\sum$input + reaction heat	q	-38.32

dynamics to neural nets and statistics. Data reconciliation adjusts the original masses and analysis systematically by iteratively closing the mass and energy balance. The variation of the data is not performed by randomly but is subject to the known uncertainties (standard deviations) in the data. The experience of the plant personnel is incorporated in the calculation as is measurement and sampling error. Immeasurable data are initially guesstimated from plant experience and their values are subsequently iteratively estimated within the data reconciliation theoretical framework. Therefore, the adjustments made on plant data can also be used as soft sensors for data that cannot be measured directly or it can provide an estimate for the quality of the measurements in addition to an estimator for the actual performance of the plant.

Chemical equilibrium

Thermodynamic potential and limit For a chemically reactive system, we are always concerned with under what conditions (temperature, pressure, concentration etc.) a reaction could take place (the affinity), and if it can take place to what extent it could reach (the equilibrium)? A criterion for the affinity of reaction (the possibility) and for the chemical equilibrium which is obtained is described by the second law of thermodynamics. In extractive metallurgy, including the recycling metallurgy, these questions have to be answered before any real experimental and engineering design. In recycling metallurgy, one should know for example metals are thermodynamically subject to oxidation in air at elevated temperatures (even slightly at room temperatures). This is determined by the affinity of the metal with oxygen. However, the oxidation potential and extent are determined by the partial pressure of oxygen or other oxidizing gases such as CO_2 or H_2O vapour, and by temperature. With the use of second law of thermodynamics, these can be quantitatively evaluated.

The second law of thermodynamics Whether a process such as a chemical reaction or simply the state change of a matter could take place spontaneously could be judged based on entropy or free energy as a criterion. This is answered by the second law of thermodynamics, and there are various ways to state the law. The flowing is the statement according to Kelvin and Planck:

It is impossible to construct a machine that, operating in a cycle, will take heat from a reservoir at constant temperature and covert it into work without accompanying changes in the reservoir or its surroundings.

Entropy For this purpose, another state function "entropy" S is introduced related to the heat and temperature of a system. Physically speaking, entropy represents the chaotic extent of a system. The higher the entropy for a system, the more chaotic the system is. In nature, a spontaneous process always takes place towards an entropy increase. If heat flows into a system, the change in entropy is given by $dS = \delta q/T$ (δq is an infinitesimal heat quantity and T is the absolute temperature of the system).

In a thermally insulated system, $dS = 0$ for reversible changes within the system and for irreversible changes $dS > 0$. The entropy of a thermally insulated system can never decrease. This could be used to judge whether a process is spontaneous. Entropy is an extensive thermodynamic property. In entropy calculations it is important to distinguish between the "system" and the "surroundings", and the combination of both constitutes an "isolated" system. From the definition above, entropy can be calculated in a similar way like enthalpy using C_P formulas. It is also defined that the entropy at absolute temperature "zero" K equal to "zero" for all crystalline materials in internal equilibrium (the Third Law of Thermodynamics). For most of the substances entropy at standard state of 298 K and 1 atm, the standard entropy S^o_{298}, is available in thermodynamic data-books or databases. Similar to enthalpy calculation, entropy change for a chemical reaction and variation of entropy with temperature can be determined according to the standard entropy of each substance and their temperature-dependent C_P functions.

Entropy as criterion for equilibrium The great value of the entropy function in chemistry and metallurgy is its ability to judge the direction of a process and its final equilibrium state of the process. If no heat is supplied from the surroundings, any irreversible change within the system would lead to an entropy increase, $dS > 0$, whereas for reversible changes $dS = 0$. This has been described above.

Example A.7

Calculate the entropy change of iron from room temperature ($\alpha-$Fe) to liquid iron at 1627° C (1900 K), the melting point of iron is 1539° C (1812 K). Iron experiences a number of phase transformations from room temperature to its melting point, as follows:

$$(\alpha-\mathrm{Fe})_{(s)} \overset{1033\mathrm{K}}{\rightarrow} (\beta-\mathrm{Fe})_{(s)} \overset{1183\mathrm{K}}{\rightarrow} (\gamma-\mathrm{Fe})_{(s)} \overset{1812\mathrm{K}}{\rightarrow} (\mathrm{Fe})_{(l)} \tag{A.76}$$

All the heat capacities of different structured iron are known and the enthalpy change of each phase transformation are given. The standard enthalpy of $\alpha-$Fe at room temperature is also known: $S^o_{298,\alpha-Fe} = 27.2(J/K\cdot mol)$. The entropy change of solid $\alpha-$Fe to liquid iron at 1627° C can be calculated simply from the above data.

Answer *The answer is given by Figure A.14 produced by HSC [402].*

Nobility of metals and refining All metallurgical operations deal with pure elements or solutions of elements. To process materials, there are thermodynamic constraints that

Figure A.14: The entropy change for Fe between 25 to 1627°C (1900 K)

must be taken into account. Primary metals are produced from ores that are processed and reduced to metallic form, and subsequently refined into pure metals (i.e., all impurities removed to acceptable limits). After, alloying elements may be added to obtain the desired alloy composition [397]. Recycling processes follow a similar path, which is often remelting, refining i.e. removal of minor elements and subsequently alloying to obtain final metal quality.

All chemical systems tend to the lowest possible energy state. What determines the feasibility of a reaction is the variation in the standard free Gibbs energy (ΔG should be used strictly speaking), ΔG^o; a reaction will be feasible when $\Delta G^o < 0$. The more negative ΔG^o the more complete the reaction is. In equilibrium, the variation in the standard free Gibbs energy ΔG^o can be calculated, for metal oxides, by the expression [397].

$$\Delta G^o = -RT \cdot \ln(K) = RT \cdot \ln(p_{O_2}) \tag{A.77}$$

An extract of the Ellingham diagram below shows the ΔG^o values for the oxidation of some elements and their oxides as a function of temperature. The Ellingham diagram is very useful since ΔG^o can be obtained directly at any temperature. Complete diagrams are published for oxides, sulphides and halides [397, 405], but the authors present here some simple extracts, for more clarity and useful to the discussion in this paper. Figure A.15 shows an extract of the Ellingham diagram for chlorides. Ores of reactive metals oxidise very easily and are therefore reduced in the form of halides, which is the case of aluminium, magnesium and titanium.

Graphically, the reduction of the metal with carbon will occur when the metal oxidation line crosses the carbon oxidation line, and thus the sum of ΔG^o is negative. It can be seen from Figure A.15 that at temperatures higher than about 750°C, FeO can be reduced to Fe, and that Cu can be reduced at temperatures higher than about 100°C. In the Ellingham diagram, the metals positioned at the top of Figure A.15 are said to be nobler than the ones below, since they oxidise less easily. This obviously has a large consequences for recycling and explains why copper cannot be removed from steel during converting. When a mix of

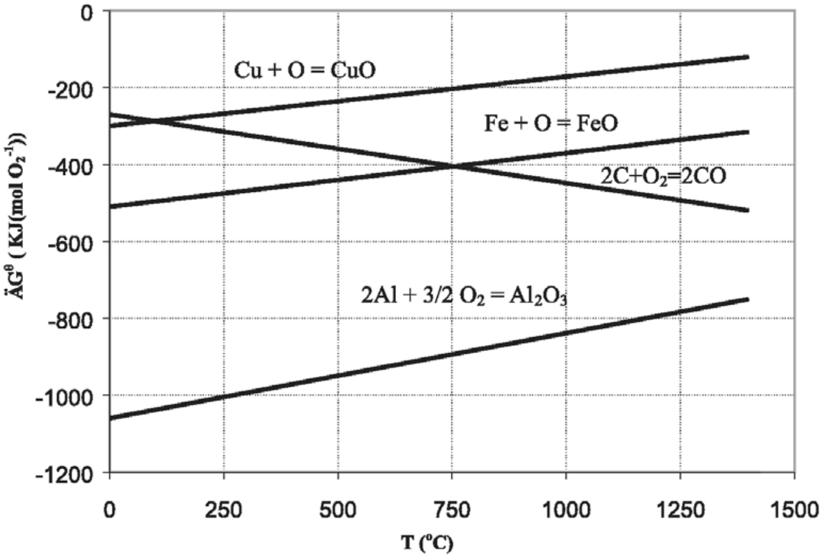


Figure A.15: Extract from the Ellingham diagram for oxides

different metals is recycled in a converter, the less noble metals will thus be oxidised and leave the process in the slag. During copper converting, oxygen is blown into the molten metal/matte at a temperature of around about 1250°C, it is clear that any aluminium or iron contaminations will be oxidised and lost to the oxide slag. Similarly, it is clear from the examination of Figure A.16, that during aluminium recycling and refining, magnesium and titanium contaminants will be lost to the chloride slag and copper and iron will remain in the molten metal.

Alloy composition, microstructures and properties Figure A.17 shows the phase diagram of the binary alloy Fe-Al [406]. The use of phase diagrams is one of the basic tools of metallurgy and material science. The properties of metallic materials depend on the amount of the various elements present and the microstructures formed during solidification and eventual thermal and mechanical treatments, to produce the optimal combination of physical and chemical properties. Figure 13 provides information about the phase transformations that the Fe-Al alloy undergoes, for changing compositions and temperatures, at a given pressure. By examination of the phase diagram, it is clear that the solubility of iron in aluminium is complete through the composition range in the liquid phase, and that the solidification temperature goes down with increasing aluminium content (see trend of "Liquidus" line). After solidification the solubility of iron in aluminium becomes very low (right side of Figure A.17) due to the formation of the inter-metallic $Al_{13}Fe_4$, with an orthorhombic crystalline structure that will precipitate for lower amounts of iron in the aluminium matrix that has a FCC (face cubic centred) structure.

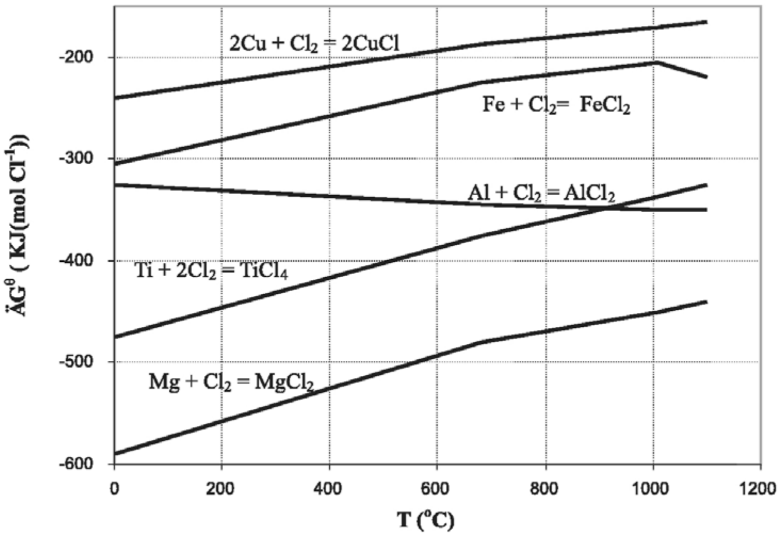


Figure A.16: Extract from the Ellingham Diagram for some chloride compounds

Solution chemistry

Iron can obviously be removed from aluminium by suitable refining, however, the phase diagram indicates that for low concentrations of Fe in Al it will be rather difficult to remove due to its low activity. This can be explained due to the interactions between the solute (minor element - Fe) and the solvent (major element - Al), the solute is either not "available" or not "active" to react or is more reactive than in the ideal situation. When minor elements (contaminants) are present is small amounts, their interactions with the solvent tend to be even stronger than at higher concentrations. The activity a, expresses this deviation from ideal situation and is given by the expression [397]

$$a_1 = N_1 \gamma_1 \tag{A.78}$$

where N_1 is the mol fraction of component 1 and γ_1 its activity coefficient (For an ideal compound, $a_1 = N_1$ and thus $\gamma_1 = 1$). The calculation of the activity gives the information about the extent to which a determined element or compound can be actually removed from the molten metal. Figure A.18 shows the activity coefficient of iron dissolved in aluminium as a function of iron content for several temperatures. The activity coefficient is in the magnitude order of 10^{-4} in the temperature range 700°C - 800°C which are typical refining temperatures of aluminium alloys. Therefore to remove the small mounts of diluted iron from the molten aluminium is very difficult.

Iron is an alloying element in aluminium alloys in only a few specific cases, and it is the most common contaminant of these alloys [407]. The maximum amount of contaminants in aluminium alloys allowed can be as low as 0.15 wt.%, with the maximum amount of each separate contaminant being 0.05 wt.%, according to industrial standards (VDS, 2000). This range exists since it leads to a decrease of physical properties [407]. For slow cooling conditions

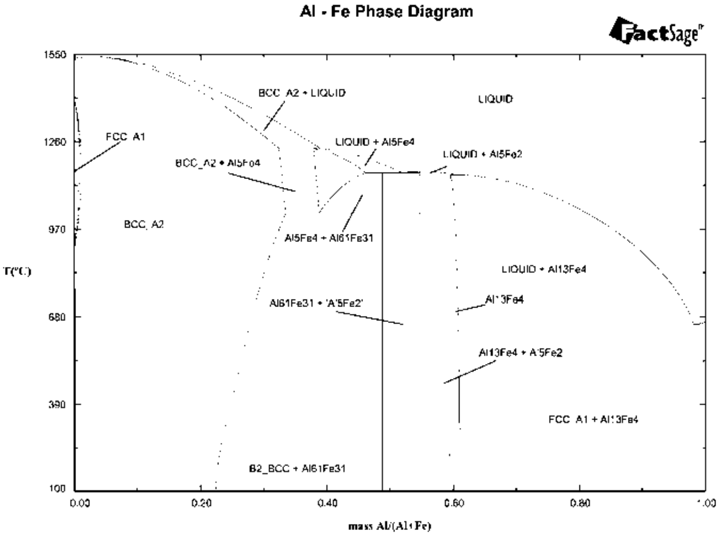


Figure A.17: Al-Fe alloy phase diagram

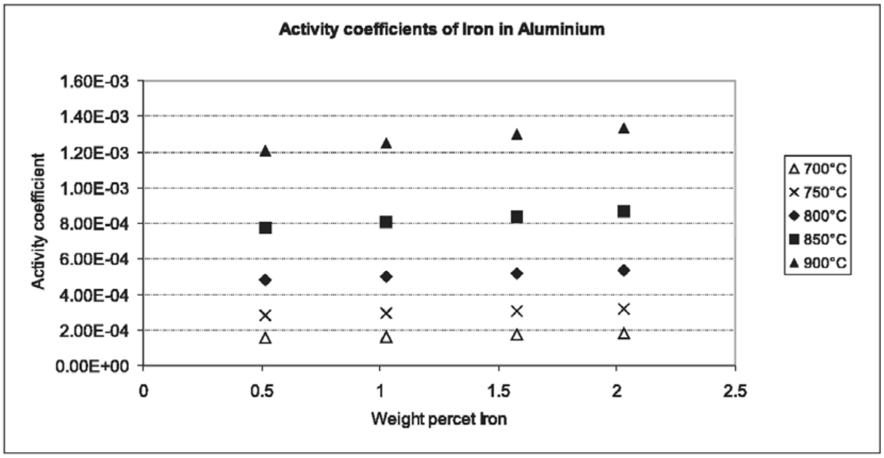


Figure A.18: Activity coefficients of iron in aluminium derived from phase diagram

(i.e., normal industrial conditions) elongated needle-like grains of $Al_{1}3Fe_{4}$ (Figure A.17) will form that act as microscopic stress concentrators in the metal decreasing further all properties by as much as 50% [407]. Therefore the presence of iron in aluminium alloys can compromise its application and thereby its economical value. Therefore, if the iron contamination is above those values, primary aluminium must be added to the recycled metal to match the composition requirements. This contamination leads therefore to depletion of resources and extra recycling costs, since iron has to be removed or diluted with.

A.2.3 Exergy: Measure of the quality loss of recycled materials

Exergy and resource efficiency

The combination of the first and second law of thermodynamics lead to the definition of the concept of exergy, introduced by Rant in 1953 [408] [409]. The exergy of a particular energy carrier (energy or matter) indicates its potential or capacity to produce work, i.e., to cause changes in the local environment. The exergy of a system can be defined by the general equation (Kotas [410]):

$$\dot{E} = U_1 - U_2 - T_o \cdot (S_1 - S_2) \quad [J] \tag{A.79}$$

where U is the internal energy of the system.
Exergy (E) consumption is related to the sum of the entropy produced (Kotas [410]):

$$\Delta \dot{E} = T_o \cdot \sum \Delta S \ [J] \tag{A.80}$$

where T_o is the reference temperature and ΔS is the entropy of the system. A more detailed treatment of the exergy formulas is out of the scope of this work; it can be found in the works of Kotas [410] and Szargut [411]. When resource depletion is discussed, one can argue that what is consumed is neither matter nor energy, but useful energy, i.e., the exergy content of resources [408]. It can be therefore stated that Exergy is the ultimate limiting resource. In this view, the exergy losses in product systems can serve as a measure of "exhaustion", and thus of the efficiency of resource use of product systems. A practical difficulty of exergy analysis is that it requires the definition of a reference state. A characteristic of the natural systems is that the reference state is particularly difficult to define and does not comply with the requirements of a theoretical reference state: it is not in equilibrium and has local and time gradients. In this article, the reference state defined by Szargut [411] will be used.

Exergy content of materials

The structure of materials determines its properties, and thus the usability of materials for a determined purpose. A useful material normally has lower entropy than the surroundings [411]. When materials can no longer suite a certain use due to the decrease of properties, its "quality" is said to be lower. This lower quality is due to the fact that the atoms in the materials structure are then arranged in such a way that its properties decrease. When contaminations are introduced in materials during recycling, the entropy of the materials increases because the contaminant will mix, interfering in the material's structure and sometimes also reacting with the other compounds, therefore originating a "less ordered" structure. The phase diagram shown in Figure A.17 illustrates the changes in structure of the binary alloy (i.e. binary mix) Aluminium-Iron, as a function of composition and temperature. Exergy (E) is a thermodynamic measure for the change in the structure of materials. Therefore, exergy losses can describe the quality losses of materials during recycling. For specific applications, Eq. A.80 can be further developed into many forms. For application to the calculation of the exergy content of resources, the chemical exergy is the component of interest. The chemical exergy content for mixtures can be calculated by [411]

$$\dot{e}_{mixture} = \sum n_i \cdot \dot{e}_i + RT_o \cdot \sum \dot{e}_i \cdot \ln(a_i) \quad [J/kg] \tag{A.81}$$

where e is the specific exergy (content per mass unit) of component i, R is the gas constant, T_o is the temperature in the reference state, n_i is the mol or mass fraction and a_i is the activity of component "i" in the mixture. This equation is used in the calculation of the exergy content of metals alloys and to account for the exergy losses due to the change in composition as a consequence of contamination. LCA-based methods have been developed to calculate the exergy content of several types of materials such as ores and metals (Finnveden and Östlund [408]). Table A.9 shows the exergy content of some metals, using the reference state proposed by Szargut [411]. The quality losses during recycling can be described by the loss of exergy content of the material.

Table A.9: Specific chemical exergy content of some metals (Finnveden and Östlund [408]) recycling dilution losses

Material	Exergy [MJ/kg]
Iron	0.88
Copper (Sweden)	990
Lead	13
Zink	19
Aluminium	4.1
Platinum	5800
Gold	3500000

Model for the calculation of exergy changes during recycling

For the calculation of the exergy changes during recycling, the authors focused on metal alloys, as these are the most relevant materials in passenger vehicles, from an environmental perspective. When metals are recycled, different types of losses occur. These losses can be classified into processing losses, solution and dilution losses. The losses during the metallurgic recycling of metals can be classified in three different types: first order, second order and third order losses. The first order losses correspond to the amount of material that is lost to landfill after shredding and separation, and lost in the slag during smelting. The first order losses result in a decrease in the exergy content in the system due to the loss of matter. These losses can be directly calculated using equation A.81 by multiplying the specific exergy of each component in the material lost by the mass of lost material. The second order losses occur during smelting. When contaminants are present, they dissolve in the molten metal, increasing the entropy of the alloy (i.e. increasing the disorder of the system). This will ultimately result on a loss of properties of the recycled alloy, compared to the primary alloy, therefore the second order losses are the quality losses of the system. The second order loss corresponds to an exergy loss due to increase in the disorder of the system (and not to a loss of mass). The second order losses occurring during smelting can be calculated adapting Eq. A.81 to:

$$\begin{aligned}\Delta \dot{E}_{mixture} = {} & \left(\sum m_i \cdot n_i \cdot \dot{e}_i + RT_o \cdot \sum m_i \cdot \dot{e}_i \cdot \ln\left(a_i\right)\right)_{input} - \\ & \left(\sum m_i \cdot n_i \cdot \dot{e}_i + RT_o \cdot \sum m_i \cdot \dot{e}_i \cdot \ln\left(a_i\right)\right)_{output} \quad [J]\end{aligned} \tag{A.82}$$

where m_i is the mass of each component, and "input" and "output" refer respectively to the state before and after the smelting operation.

The third order losses are due to the eventual need for dilution of the contaminants, when they exceed the maximum content allowed for a specific alloy. Additional high purity resources must be added to dilute the contaminant to an acceptable level or original level. This leads to the depletion of the resource reserves and decreases the resource efficiency of the system. Third order losses can be directly calculated using Eq. A.81 by multiplying the specific exergy of each component of the dilution material by the mass of dilution material required. To calculate the activities of the components of non- ideal solutions in Eqs. A.81 and A.82, the behaviour of the components in the solution must be known. The activity of the components varies strongly with the composition, pressure and temperature. With the use of solution models, it is possible to calculate the activity of multi-component solutions. Different solution models have been developed, according to the behaviour of the components in the solution (Sano [412]): (i) Regular Solution model: Substitutional solutions; (ii) Sublattice Solution model: Interstitial solutions, intermetallic phases and ionic liquids; and (iii) Quasichemical Solution model: Non-random mixing (see Figure A.18). A measure of the efficiency of resources use in the products life cycles can be defined as Resource Input ratio, "RI" This measure accounts the ratio between the resource inputs required for dilution during recycling and the input material to be recycled as shown by Eq. A.83.

$$RI = \left(\frac{\dot{E}_{input}}{\dot{E}_{initial}}\right) \tag{A.83}$$

Exergy calculation example

By knowing the amounts of liberated and not liberated material in the scrap to melt, a mass balance allows the calculation of the composition of the alloy produced by smelting the mixture of liberated and not-liberated metal. The Factsage software calculates the activities of all compounds in the solution, known the temperature, pressure and mass fractions. With the activity data and mass fraction, the total exergy content of the alloy can be calculated using Eq. A.81 and the losses can be calculated using Eqs. A.81 and A.82. The example illustrates the effect of contaminations on the exergy content of recycled materials.[409] Suppose that a wrought aluminium scrap has the composition: 121 kg of aluminium scrap containing 1 kg of steel contamination. The aluminium in the scrap is alloy 2036. During the recovery processes, 10% of the aluminium is estimated to be lost during recovery and separation (for simplicity of the example, and not unrealistically, it is estimated that only the aluminium is lost), remaining thus 109 kg of aluminium scrap containing 1 kg of steel (for simplification of the example, the steel composition is considered to be 100% Fe). This will be called mix 1. The alloy produced by smelting of the scrap will be called alloy 2. With the recovered material, a cast aluminium alloy type 380 will be produced, because of the higher iron content allowed for this alloy. The two alloy compositions:

- Al 2036 alloy (wrought Al alloy): Al 96.6%, Cu 2.6%, Si 0.5%
- Al 380 alloy (cast Al alloy): Al 89.4%, Fe 0.8%, Mg 0.2%, Mn 0.4%, Si 8%

By calculating the limiting iron content allowed i.e. 0.8%, an amount of 17 kg of pure wrought aluminium 2036 must be added to dilute the iron contamination. The alloy produced after dilution will be called alloy 3. The data and composition of the alloys can be seen in Table A.10. The typical melting temperature for aluminium is about 750°C and the pressure is the atmospheric pressure. Introducing these data in the Factsage software, the activity of the several elements was calculated. The activities are given in Table A.11. Table A.12 shows the specific exergy content of each alloy produced, the total exergy content ($\dot{E}$), and the first, second and third order exergy losses. The first order losses correspond to the 10% loss of alloy 2036 during recovery and recycling. The second order exergy losses correspond to the decrease in specific exergy $\dot{e}$ due to the solution of contaminants, accounting for a total of 55.3 MJ. The third order losses correspond to the amount of exergy added to the system as dilution material. From Table A.12, it is clear that the specific exergy content $\dot{e}$, decreases from Alloy 1 to Alloy 3, therefore, the material loses quality during the smelting and dilution processes. Finally the resource efficiency value was calculated for the smelting and dilution, being the sum of the exergies contained in Alloys 1 and the Dilution alloy, while the exergy content of Alloy 4 and $\dot{E}$ is the sum of all losses. The resource input ratio obtained for this example was RI=0.16. The resource efficiency calculated according to:

$$\Psi = \frac{\left(\dot{E}_{out} - \dot{E}_{loss}\right)}{\dot{E}_{in}} = 0.88$$

Just for an indication of how large the contamination problems can become, if secondary alloy 2036 was to be produced from the contaminated scrap, having a maximum iron content of 0.3%, the dilution material required would be 230 kg of not contaminated alloy 2036, or alternatively 220 kg of pure aluminium (99.9%). This is why in the industrial practice the recyclers have a relatively large scrap stock with different compositions that they mix, to avoid the need for dilution with high purity materials during the production of recycled alloys.

Additionally, it must be mentioned that not all losses are accounted yet. To produce alloy 380 with the required composition, some silicon, magnesium and manganese must still be added to the molten metal, leading thus to additional exergy losses, and some copper contamination remains, as copper cannot be removed from the molten aluminium by current industrial processes.

Table A.10: Amount and composition of the different alloys

Alloy	Mixture	Mass (kg)	Chemical composition			
			Al	Cu	Fe	Si
Mix 1	Al2036 Fe	108 1	0.969 0.000	0.026 0.000	0.000 1.000	0.005 0.000
Alloy 2	melt	109	0.959	0.026	0.009	0.005
Dillution alloy	Al2036	17	0.969	0.026	0.009	0.005
Alloy 3	Al380	126	0.961	0.026	0.008	0.005

Table A.11: Activities of the solutes in liquid aluminium, of the alloys obtained

Alloy/Mix	Activity solute (750^o,1atm)		
	Cu	Fe	Si
Alloy 1	0.666	-	0.0012
Alloy 2	0.666	$3.4\cdot10^{-6}$	$2.65\cdot10^{-5}$
Alloy 3	0.666	$2.4\cdot10^{-6}$	$2.66\cdot10^{-5}$

Table A.12: Exergy content and exergy losses due to the iron contamination

Material	$\dot{e}_{mixture}$ (MJ/kg) 1	Mass (kg) 2	$\dot{E}_{mixture}$ (MJ) 1x2	Losses $\dot{E}$(MJ)		
				1st order	2nd order	3rd order
Alloy1	32.105	120	3852.6	385.3		
Mix 1 (Al) Mix 1 (Fe)	32.105 6.7398	108 1	3467.3 6.7			
Alloy 2	32.074	109	3496.1		22.0	
Dillution alloy	32.105	17	545.8			545.8
Alloy 3	31.893	126	4018.5		23.3	

A.3 Computational fluid-dynamics modelling

Metallurgical processes involve complex phenomena of momentum, heat and mass transport, which play important roles in reaction kinetics and reactor performance. Process simulation by using CFD software can give detailed information of fluid flow, heat and mass transfer in metallurgical reactors, so as to achieve a better understanding of the process. During the past two decades, the CFD codes have been developed considerably, and the CFD simulation has been applied for process modification and new process development. Together with the rapid growth of computer speed and capacity, the applications of CFD in research and development for metallurgical processes will in future become more popular in universities, research institutions, and even in industry.

This chapter will give an overview about CFD principles, its capabilities, the available software packages, and general simulation procedures. Modelling examples in metallurgical processes from both literature and authors' own work have been presented in Part IV. Work by the authors include transport phenomena in copper and nickel flash smelting, blast furnace ironmaking, HIsmelt ironmaking, ladle refining and continuous casting of steel, metallurgical waste-heat boilers, as well as a rotary-kiln waste-incinerator.

A.3.1 Introduction

CFD and its capabilities in modelling industrial processes

CFD refers to Computational Fluid-Dynamics. In short, CFD is a numerical modelling tool to simulate fluid flow related processes. In CFD, the governing Partial Differential Equations are numerically solved for the conservation of mass, momentum, heat and chemical species in the fluid-flow systems. As a result, CFD modelling generates the detailed distribution of velocity, temperature, concentration of species, and other flow-related variables in all dimensions of the whole flow domain. CFD has entered into process industries for a long time and is playing an increasing role not only as a research tool, but in the optimization and development of industrial processes and products. The aerospace industries were the early target for CFD applications in design, R&D and manufacture of aircraft and jet engines since the 1960s. More recently since 1980s, other industrial areas such as automotive, energy, chemical and metallurgical industries have found more and more CFD applications. The following is a partial listing where CFD has found applications:

- Aerodynamics of aircraft and vehicles
- Hydrodynamics of ships
- Power plant: combustion in furnaces, boilers and gas turbines
- Turbomachinery: flows inside rotating passages, etc.
- Electrical and electronic engineering: cooling
- Chemical process engineering: mixing and separation, reactor optimization
- Metallurgical engineering: single and multi-phase flows in furnaces, heat transfer and chemical reactions, cooling and purification of the flue gases, etc.
- Buildings: heating, ventilation, wind loading
- Hydrology and oceanography: flow in rivers, estuaries (mouths of rivers), oceans

- Metrology: weather prediction/forecasting
- Bioengineering: blood flows in arteries and veins

Good references are available for the introduction of CFD and CFD methods, and examples are books "Numerical Heat Transfer and Fluid Flow" by Patankar [413], "An Introduction to Computational Fluid Dynamics: The Finite Volume Method" by Versteeg and Malalasekera [414], and articles by Singhal [415] and by Schwarz [416, 417].

Relationship of CFD with other process modelling tools

There are two general approaches to process modelling: (1) **first principle approach**, and (2) **functional block approach**. In the **first principle approach**, the models are derived based on physical and chemical laws, e.g. mass and energy balances, thermodynamics, reaction kinetics, mass and heat transport theories, and therefore have better interpolation and extrapolation abilities. This approach is often used for process understanding, development, design and optimization. CFD modelling falls into the models of the first principle. The **functional block approach** is often referred to as **black box approach**, in which the models are derived based on empirical descriptions. With this approach, a standard mathematical structure is first assumed for the model, and then the parameters of the model are specified in a way that the model calculation results best fit the measurement data of a real process, without physical chemical analysis of the process. For instance, in industrial operation, existing operating data are often related to the controllable parameters using generic mathematical models such as multivariable analysis, pattern recognition and neural network to optimise the process operations. If the black box model is a dynamic model which reflects the time transient response of the process from one steady state to another, the method for fitting the model parameters using a sequence of process input and output data is usually called "Identification" and the obtained model is called an "identification model". These process dynamic models are used in model based predictive control, adaptive and self-tuning control. In most cases, a complete process model building is never entirely based on a single approach. For example, a process model based on the first principle approach usually leaves a few parameters to be validated by experiments or industrial operating data. In CFD modelling, e.g. turbulence is usually modelled with empirical parameters, which have to be justified to different flow situations through experiments. In heat transfer problems, heat transfer coefficient or radiation parameters partially or purely come from experimental data with empirical formulas. On the other hand, the mathematical structure of an identified process model should be assumed based on the understanding of the physico-chemical nature of the process. In general, the more the fundamental theories can be embodied in a model, the better the model will be. In simulating an industrial process such as chemical or metallurgical, different simulation tools are available for various purposes [418, 419, 420]. The examples can be listed as follows:

- Thermodynamic modelling: Thermodynamic modelling calculates the phase equilibria, chemical reaction equilbria, etc. Examples of commercial packages include MTDATA ®(www.npl.co.uk/npl/cmmt/mtdata), ChemSage ®(gttserv.lth. rwth-aachen.de/s̃p/tt/chemsage/chemsage.htm, successor of SOLGASMIX), FactSage ®(www. factsage.com, a combination of FACT-Win and the calculational routines of ChemSage for wide range applications of computational thermochemistry since 2001) , F*A*C*T ®(www.crct.polymtl.ca/fact), HSC (www.outokumpu.com/hsc) , Thermo-Calc ®(http:// www.thermocalc.se), Lucas. etc. They are based fully on the thermodynamic laws, and utilize the principle of free energy minimisation, although many data e.g. activity coefficients are obtained from experiments. They could handle wide range of metallurgical applications such as alloys, slags, matte, and aqueous solution systems

- Kinetic modelling: Kinetic modelling should be based on the first principles of laws of physical chemistry. However, many parameters have to be obtained by way of experiments, e.g. the rate constant, mass transfer constant, etc. Even the rate equations of many reactions have to be determined by experiments. However, they follow certain rules. One well known software package for kinetic modelling is CHEMKIN ®(www.ca.sandia.gov/chemkin) . It is a software package to facilitate the formation, solution, and interpretation of problems involving elementary gas-phase and gas-surface heterogeneous chemical kinetics.
- Flowsheet simulation: Flowsheet simulators calculate materials flows of streams, heat and energy requirements of unit operations, and size and cost of equipment with considerations of recycle streams and user given design specifications. The basis of the flowsheet simulation is mathematical models of their underlying chemical and physical phenomena as well as overall heat and mass balances. Flowsheet simulators are with mixed approaches of first principle models and black box models. Examples are USIM Pac ®(www.processeng.com/brgm.asp), METSIM ®(members.ozemail.com.au/ozmetsim/met2), Aspen Plus (www.aspentech.com), PYROSIM ®(www.mintek.co.za/Pyromet/Pyrosim/ Pyrosim.htm) etc.
- Process control modelling: Expert systems, Neural network, etc. Process control modelling is more based on black box models, or gray box models.
- CFD modelling: CFD modelling is based on the first principle approach of conservation laws of mass, momentum, energy, etc. However, there are various empirical submodels, parameters and constants needed to complete the modelling. Examples of CFD packages are PHOENICS ®(www.cham.co.uk), CFX (www-waterloo.ansys.com/cfx), FLUENT ®(www. fluent.com), FIDAP ®(www.fluent.com) , Flow-3D ®(www.flow3d.com), STAR-CD ®(www.cd-adapco.com). They are all general purpose codes, and can handle most of the flow related problems. There is a trend to couple the chemical reactions, thermodynamic database and kinetic models into the flow system. All the packages mentioned above can handle, to certain extent, various types of homogeneous and heterogeneous chemical reactions. Simulation of fuel combustion reactions (gas, liquid, coal) is a large area where CFD has addressed broadly and devoted to from chemical reaction point of view. For example, PHOENICS has introduced the Chemkin interface to its flow solver. FLUENT has its general module for homogeneous chemical reactions, and the recent announcement (21 November 2003, www.fluent.com) about the coupling Aspen-Plus to Fluent is a clear indication. In addition, there is also a trend to couple the stress analysis in solid to CFD simulation, the Fluyid-structure analysis. PHOENICS has introduced fluid- stress analysis for some years, and recently Fluent-ABAQUS initiative (22 December 2003, www.fluent.com) and ANSYS-CFX merging are clear indication of the strong need and development of this multi-physics simulation.

CFD in metallurgical processes

Metallurgical processes involve the extraction of metals from different types of minerals, e.g. from iron to wrought iron, from wrought iron to steel; from copper concentrates to pure copper. The processes involve various types of materials flow in solids, liquids, gases, and their mixtures, from one part of the equipment to another, and from one equipment to another equipment. Metallurgical processes are normally complicated due to its multi-phase, high temperature, and highly reactive nature. But, the metallurgical processes are well suited for simulation with CFD, because most of the materials are flowing either as continuous or as dispersed phases. CFD has been found useful in studying various metallurgical processes, and various aspects of a specific process. It can be used for 1) insight understanding of an existing process, 2) modification and optimization of the operation and design in an existing process, and 3) new process development. Looking into the modelling activities globally and from the literature, it can be found that most of the unit operations have been modelled more or less with CFD. Some are with over 20 years history such as in ladle metallurgy and continuous casting of steel. Some are just in the beginning such as in various smelting processes for ferrous and non-ferrous metals and hydrometallurgy. The following is a partial list where CFD has been used in the modelling different metallurgical process.

- **Nonferrous smelting processes**: Flash smelting, Hall-Hérout Cell, PS-converter
- **Iron and steelmaking**: Blast furnace, HIsmelt, BOF, EAF
- **Ladle metallurgy**: gas-stirring, electromagnetic stirring
- **Continuous casting of steel**: tundish, casting mould
- **Off-gas cooling, dust precipitation**: waste-heat boilers, cyclones, electrostatic precipitators
- **Hydrometallurgy**: stirring tanks, thickeners, tank-house

Good comprehensive books and review articles are available for the application of CFD in process metallurgy, and here are some of those: Schwarz [416, 417, 421], Johansen [422], Szekely [423, 424, 425], Evans [426], Guthrie [394] for articles; Szekely and Themelis [427], Szekely [428], Szekely, Evans and Brimacobe [429], Sano et al. [412] for monographic books.

A.3.2 Basic principles of CFD

This chapter is devoted to introduce basic concepts about CFD. The topics include: the theoretical background - the governing partial differential equations in relation to the finite-volume method, the solution procedures, some specific issues in modelling industrial application processes: turbulence, multi-phase flow, and thermal radiation; introduction to several commercial CFD packages used in many applications; and a brief presentation of modelling procedures as a general guideline. The information provided in this chapter, especially the governing partial differential equations is just to show what is really behind the flowing behaviour of fluids, and a review of various conservation laws of physics and chemistry. With this basic knowledge in mind, you will understand what you are modelling when using a commercial package and feel your future modelling activities are well grounded.

Governing equations and the solution procedures

Governing partial differential equations In processes involving fluid flow and heat and/or mass transfer, the fluid behaviour is basically governed by a set of partial differential equations (PDEs), representing the conservation of mass and momentum (the Navier-Stokes equations), thermal energy and chemical species. The governing equations represent mathematical statements of the **conservation laws of physics.**

We start with laminar flow system, though most of the flow in engineering applications is turbulent. For turbulent flow system, the governing PDEs take almost the same form as those of the laminar system, with some additional terms. We will present the PDEs for turbulent flow system later in comparison with the laminar flow system. The following presentation is based on the **Finite Volume Method** (FVM) , in contrast to other methods such as **Finite Difference Method FDM** (FDM), **Finite Element Method** (FEM), and **Spectral Method** , because of its popularity in most of available commercial CFD codes. Actually, FVM is a special finite difference formulation. Different textbooks may use different notations and ways of derivation for these conservation equations. But the meaning and results should always be the same. We follow more or less the notations from Versteeg and Malalasekera [414]. It should also be noted that we almost omitted all the derivation procedures. The interested readers can always look into details in the references.

- **The continuity equation for the mass conservation**: The rate of change of the density (mass per unit volume) equals the net flow of mass into the element cross its boundaries.

  $$\frac{\delta \rho}{\delta t} + div(\rho \mathbf{u}) = 0 \tag{A.84}$$

  Rate of increase of mass in fluid element = Net rate of flow of mass into fluid element

  $\frac{\delta \rho}{\delta t}$: rate of increase of mass in fluid element

  $-div(\rho \mathbf{u})$: net rate of flow of mass into fluid element

  For incompressible fluid, the density constant $\left(\frac{\delta \rho}{\delta t} = 0\right)$, and the continuity equation becomes: $div(\mathbf{u}) = 0$, i.e. $\frac{\delta u}{\delta x} + \frac{\delta v}{\delta y} + \frac{\delta w}{\delta z} = 0$.

- **The equation of motion for the momentum conservation, or called the Navier Stokes equation**: the rate of change of momentum equals the sum of the forces acting on a fluid particle (**Newton's second law**). For x-momentum equation, it can be written in the following form:

  $$\frac{\delta}{\delta t}(\rho u) + div(\rho \mathbf{u} u) = div(\mu\, grad\, u) - \frac{\delta p}{\delta x} + S_F \tag{A.85}$$

  Rate of momentum increase of the fluid element = Net rate of momentum into the fluid element + Sum of forces acting on element

  $\frac{\delta}{\delta t}(\rho u)$ rate of increase of the fluid element

  $-div(\rho \mathbf{u} u)$ net rate of momentum into the fluid element

$div(\mu\, grad\, u)$	surface force on the element due yo viscous stress
$\frac{\delta p}{\delta x}$	surface force on the element due to pressure gradient
S_F	different body forces - gravity, centrifugal, Coriolis or electromagnetic forces

- **The equation of enthalpy for thermal energy conservation**: The rate of change of energy equals the sum of the rate of heat addition to and the rate of work done on a fluid particle (**first law of thermodynamics**).

$$\frac{\delta}{\delta t}(\rho h) + div(\rho \mathbf{u} h) = div(k\, grad\, T) + \frac{dp}{dt} + \Phi + S_h \tag{A.86}$$

with

$$\begin{aligned}\Phi \quad = \quad & \mu \left(2 \left[\left(\frac{\delta u}{\delta x}\right)^2 + \left(\frac{\delta v}{\delta y}\right)^2 + \left(\frac{\delta w}{\delta z}\right)^2 \right] + \left(\frac{\delta u}{\delta y} + \frac{\delta v}{\delta x}\right)^2 \right. \\ & \left. + \quad \left(\frac{\delta u}{\delta z} + \frac{\delta w}{\delta x}\right)^2 + \left(\frac{\delta v}{\delta z} + \frac{\delta w}{\delta y}\right)^2 \right) - \frac{2}{3}(div\, \mathbf{u})^2 \end{aligned} \tag{A.87}$$

Rate of increase of enthalpy in fluid element = Convective heat into the element + Conduction heat into the element +

Pressure work + Mechanical work + Other sources

$\frac{\delta}{\delta t}(\rho h)$	rate of increase of enthalpy in fluid element
$-div(\rho \mathbf{u} h)$	convective heat into the element
$div(k\, grad\, T)$	conduction heat into the element
$\frac{dp}{dt}$	pressure work
Φ	dissipation function which includes all the effects due to viscous stresses. It represents the conversion of mechanical energy to heat or internal energy in the process of deformation of the fluid due to viscosity. It has a very complicated form as shown in Eq A.87
S_h	other sources

- **The equation of chemical species or concentration**: The rate of change of the mass of the chemical species per unit volume is equal to the rate of generation of the chemical species per unit volume minus the convection and diffusion fluxes per unit volume. If the diffusion flux is expressed by the Fick's law of diffusion: $J_n = -\Gamma_n\, grad\, C_n$. Here C_n is the mass fraction of species n.

$$\frac{\delta}{\delta t}(\rho C_n) + div(\rho \mathbf{u} C_n) = div(\Gamma_n\, grad\, C_n) + R_n \tag{A.88}$$

Rate of increase of species n into fluid element	−	Net rate of flow of species n into the fluid element du to convection	+	Rate of increase of species n into the fluid element due to diffusion	+

Rate of increase of species n into the fluid element due to sources

$\frac{\delta}{\delta t}(\rho C_n)$	rate of increase of species n into fluid element
$div(\rho \mathbf{u} C_n)$	net rate of flow of species n into the fluid element du to convection
$div(\Gamma_n\, grad\, C_n)$	rate of increase of species n into the fluid element due to diffusion
R_n	rate of increase of species n into the fluid element due to sources

- **Equation of state**: In order to close the system of fluid dynamic equations, it is also necessary to supply relationships between the thermodynamic variables as well as to relate the transport properties to the thermodynamic variables. The equations utilized are known as equations of state. Examples of these relations for a perfect gas are:

$$p = \rho RT \tag{A.89}$$

$$h = C_p T \tag{A.90}$$

$$\sum_{n=1}^{N} C_n = 1 \tag{A.91}$$

where R is the gas constant.

Governing partial differential equations for turbulent systems For the turbulent flow systems, it is the time-mean behaviour of these flows that is usually of practical interest. Therefore, the equations for unsteady laminar flow are converted into the time-averaged equations for turbulent flow by an averaging operation in which it is assumed that there are rapid and random fluctuations about the mean value. In turbulent flow systems, the flow variable ϕ (ϕ can represent the velocity components u_i, pressure p, enthalpy h, density ρ, etc.) can be time-averaged and expressed with a mean (with overbar,$\overline{\phi}$) and fluctuation components (with prime,ϕ')(also called Reynolds averaging and decomposition):

$$\overline{\phi} \equiv \frac{1}{\Delta t}\int_{t_0}^{t_0+\Delta t} \phi dt \tag{A.92}$$

and

$$\phi = \overline{\phi} + \phi' \tag{A.93}$$

It requires Δt to be large compared with the time scale of turbulent motion, but small with respect to the time scale of the mean motion in transient problems. The additional terms arising from this operation are the so called Reynolds stresses $(-\overline{\rho}\overline{u_i'u_j'})$, turbulent heat flux $(-\overline{\rho}\overline{u_i'h'})$, turbulent flux of species $(-\overline{\rho}\overline{u_i'C_n'})$, etc. To express these fluxes in terms of the mean properties of the flow is the task of a turbulence model. The following is a representation of the governing equations for a time-averaged turbulent flow system. For weak density fluctuation, the direct effect of compressibility on turbulence can usually be neglected in the time-averaged PDEs. Thus, the time-averaged equations for the conservation of mass and momentum, energy and chemical species for Newtonian fluid can be expressed in the following Cartesian-tensor form in contrast to the equations of A.84 to A.88 in the laminar flow system.

- **The continuity equation**:

$$\frac{\delta\overline{\rho}}{\delta t} + \frac{\delta}{\delta x_j}\left(\overline{\rho u_j}\right) = 0 \tag{A.94}$$

- **The equation of motion:**

$$\begin{aligned}\frac{\delta}{\delta t}(\overline{\rho u_i}) - \frac{\delta}{\delta x_i}(\overline{\rho u}_i\overline{u_i}) &= -\frac{\delta\overline{p}}{\delta x_i} + \frac{\delta}{\delta x_j}\left(\mu\left[\left(\frac{\delta\overline{u}_i}{\delta x_j} + \frac{\delta\overline{u}_j}{\delta x_i}\right)\right.\right.\\ &- \left.\left.\frac{2}{3}\delta_{ij}\frac{\delta\overline{u}_k}{\delta x_k}\right] - \overline{\rho}\overline{u_i'u_j'}\right) + S_F\end{aligned} \tag{A.95}$$

S_F is the source term and may include gravity force, magnetic force and other body forces.

- **The equation of enthalpy**:

$$\frac{\delta}{\delta t}(\overline{\rho}\overline{h}) + \frac{\delta}{\delta x_j}(\overline{\rho u}_j\overline{h}) = \overline{\frac{dp}{dt}} + \frac{\delta}{\delta x_j}\left(\lambda\frac{\delta\overline{T}}{\delta x_j} - \overline{\rho}\overline{u_j'h'}\right) + \overline{\Phi} + S_h \tag{A.96}$$

Where $\overline{\Phi}$ is the dissipation function for turbulent flow system, and takes the similar form to that of the laminar flow system if the fluctuating terms are small. $\overline{\frac{dp}{dt}}$ is the mean substantial derivative of pressure (the pressure work). S_h is the source term for enthalpy, which may result from thermal radiation, chemical reactions etc.

- **The equation of chemical species**:

$$\frac{\delta(\overline{\rho}\overline{C}_n)}{\delta t} + \frac{\delta(\overline{\rho u}_i\overline{C}_n}{\delta x_i} =)\frac{\delta}{\delta x_i}\left(\Gamma_n\frac{\delta\overline{C}_n}{\delta x_i} - \overline{\rho u_i'C'_n}\right) + S_{\overline{C}_n} \tag{A.97}$$

where $S_{\overline{C}_n}$ is the source term accounting for the rate of the creation or consumption of species in chemical reacting flows, or the rate of species creation from another phase. From above PDEs, we can see significant mathematical similarities among them in forms.

All these equations can be cast into a general form in Eq. A.98 where ϕ is a general flow variable.

$$\frac{\delta}{\delta t}(\rho\phi) + div(\rho\mathbf{u}\phi) = div(\Gamma_\phi\, grad\,\phi) + S_\phi \tag{A.98}$$

In words, it can be expressed as:

Rate of increase of ϕ of fluid element	+	Net rate of flow of ϕ out of fluid element du to convection	=	Rate of increase of ϕ due to diffusion	+	Rate of increase of ϕ due to sources

It clearly highlights the various transport processes: on the left hand side (1) the rate change term or the transient term, (2) the convective term; on the right hand side (3) the diffusive term, and (4) the source term. In order to bring out the common features, some terms not shared among the equations are included in the source terms. Note that Γ_ϕ is the diffusion coefficient, and in turbulent flow system it is the effective exchange coefficient and is the sum of laminar and turbulent counterparts. Equation A.98 is used as the starting point for computational procedures in the finite volume method. By setting ϕ equal to 1, u, v, w, and h and selecting proper values for diffusion coefficient Γ and source terms, we can get PDEs for mass, momentum, enthalpy and chemical species conservation.

Solution procedures Here, is a brief overview on the solution procedures for a general CFD problem, and they can be divided into the following steps, and the more details can be found in books of Patankar [413] and Versteeg and Malalasekera [414].

- Discretisation of the flow domain:
  - generating large number of cells or control volumes
- Discretisation of PDE's: FDM, FVM, FEM
  - generating algebraic equations for each cell
- Solution:
  - SIMPLE algorithm and its derivatives: for pressure - velocity linkage
  - TDMA line-by-line solver: for algebraic equations

First step is the discretisation of the flow domain. In practice, this divides the flow domain (to be modelled, e.g. furnace or reactors) into a large number of computational cells. The step can also be called the grid or mesh generation. Grid can be created in different ways depending on the applications. For example, with Finite-volume method, the grid can be in the following forms: (1) Cartesian grid (the cells are in rectangular forms), (2) Cylindrical-polar grid (convenient for cylindrical geometry), and (3) Body-fitted coordinate (BFC) grid, which follows the curvature of the geometry (suitable for curved geometry). With FEM method, different meshes can be generated, triangular, tetrahedral or rectangular. In order to solve the governing PDEs, the PDEs have to be integrated over each control volume in the entire flow domain. Second step is the discretisation of the governing PDEs, to form algebraic equations for each computing cell. From the generalised PDE shown in Equation A.98, four terms have to be discretised in transient cases. In steady cases, there will be only three terms to be discretised. For this purpose, different discretisation schemes are available with different level of complexity, accuracy and efficiency, especially for the convection term, from classic first-order upwind differencing scheme (UDS) and second-order central differencing scheme (CDS), to quadratic-upwind difference scheme (QUICK), which are usually used in FVM CFD codes. Here, the details on the description of those differencing schemes will not be given, and interested students can read from literature for further studies [414]. The non-linear nature of the underlying phenomena and the linkage between pressure and velocity in variable density flows requires the special treatment, and it is handled by specifically developed solution algorithm such as SIMPLE, and its derivatives (SIMPLER, SIMPLEST, SIMPLEC), and PISO etc. When studying further CFD and its methods, one will meet these terms, and further knowledge can be found in most of the CFD books such as by Patankar [413] and by Versteeg and Malalasekera [414]. In this short course, one only need to understand there are different methods available to dealing with these specific topics. The last step is the numerical solution to the sets of the algebraic equations for each cell. In CFD problems, the well-known Tri-Diagonal Matrix Algorithm (TDMA) line-by-line solver is normally used for the algebraic equations. Because of the inter-coupling of the algebraic equations, the solution has to be iterative. In CFD solutions, it is rare to get convergence without external help. Relaxation technique is usually used in the solutions by modifying the values resulting from the solver, to slow down the pace at which changes in the variables take place.

Modelling of turbulent flows

In modelling industrial processes, we quite often meet the turbulent flow, multi-phase flow, thermal radiation at high temperatures. These phenomena have not been dealt with in general treatment of flow and heat transfer processes introduced in previous section. They will be introduced in the following, to address the phenomena, the complexity, and common approaches to handle them. However, these are more advanced modelling topics, and are optional for this study. Most of the industrial processes involving fluid flow are turbulent in nature. Turbulent flows are unsteady and highly irregular in space and time, strongly diffusive, dissipative, three dimensional, and always rotational. Turbulence is an eddying motion with a wide spectrum of eddy sizes and a corresponding spectrum of fluctuation frequencies, while large and small eddies coexist in the same volume of fluid. The largest eddies are determined by the boundary conditions of the flow and their size is of the same order of magnitude as the flow domain, and the smallest eddies are determined by viscous forces. To resolve the motion of the smallest eddies numerically will require the mesh size of the numerical grid at least 10^9 in three dimensions, and it is prohibitive with the present computer capacity and speed. The treatment of the instantaneous motion with the mean motion gives a solution to the turbulent flow systems. By time-averaging the flow variables, we can get the time-averaged Navier-Stokes equations and other conservation equations. We have seen that the time-averaging process generates the fluctuation terms of Reynolds stress and heat/species fluxes due to turbulence $(-\overline{\rho}\overline{u'_i u'_j}, -\overline{\rho}\overline{u'_i h'}, \overline{\rho}\overline{u'_i C'_n}$, etc.). This causes the PDEs to be no longer a closed system. Another set of equations needs to be provided to represent the fluctuation terms. Expressing the fluctuation terms with mean flow variables is the task of turbulence modelling. Traditional way of expressing the fluctuation terms is to use the gradient - transport hypothesis, and the Reynolds stress and other turbulent fluxes are related to the velocity or other scalar gradient with the turbulent viscosity. Representation of the turbulent viscosity forms the essential part of a turbulence model. Most turbulence models adopt the eddy viscosity concept, which determines the Reynolds stresses $(-\overline{\rho}\overline{u'_i u'_j})$ in the time-averaged Navier-Stokes differential equations. The eddy-viscosity concept assumes that, in analogy to the viscous stresses in laminar flows, the turbulent stresses are proportional to the mean velocity gradients. For general flow situations, this concept may be expressed as:

$$-\rho u_i' u_j' = \mu_t \left(\frac{\overline{\delta u_i}}{\delta x_j} + \frac{\overline{\delta u_j}}{\delta x_i} \right) - \frac{2}{3}\rho k \delta_{ij} \tag{A.99}$$

Where, μ_t is the turbulent or eddy viscosity and k is the turbulent kinetic energy. In contrast to the molecular viscosity, the turbulent viscosity is not a fluid property but depends strongly on the state of turbulence. The turbulent kinetic energy k is defined as:

$$k = \frac{1}{2}\overline{u_i' u_i'} = \frac{1}{2}\left(u_1'^2 + u_2'^2 + u_3'^2 \right) \tag{A.100}$$

It is a measure of normal or diagonal turbulent stress. Based on the eddy viscosity concept, the turbulent viscosity in the flow system is proportional to the turbulent velocity scale V_s and the length scale l_m or the dissipation rate of the turbulent kinetic energy ϵ:

$$\mu_t = \rho C V_s l_m = \frac{\rho C_\mu k^2}{\epsilon} \tag{A.101}$$

and the effective viscosity is the sum of the molecular and the turbulent viscosity: $\mu_{eff} = \mu + \mu_t$. Description of the mixing length scale leads to the different turbulence models with the eddy viscosity concept. The mixing length scale can be represented by empirical prescription, by algebraic equations or by solving PDEs.

Many turbulence models based on the eddy-viscosity concept have been developed with different complexities, from zero-equation models such as the Prandtl mixing length model, one-equation models such as the Prandtl $k-L$ model, to two-equation (or multi-equation) models such as the $k-W$ model of Saffmann-Spalding, the $k-\omega$ model of Kolmogorov, and the $k-\epsilon$ models of Harlow-Nakayama and Jones-Launder. In recent years, more advanced turbulence models have been developed, and these turbulence models directly describe all the components of the Reynolds stress tensor with algebraic equations or PDEs, such as the algebraic stress model (ASM) and the Reynolds stress models (RSM). RSM solves differential equations for all Reynolds stresses and the dissipation rate of the turbulent kinetic energy. It is able to capture the non-isotropic character of the turbulence, which is present in many practical fluid flow situations such as flows with large streamline curvature, swirl or strong recirculation. The increase in the complexity of the models generally results in a better representation of the real turbulence effect. However, the computing time and capacity required are also significantly increased.

In addition, there is another level of turbulence models, called large-eddy simulations (LES). large-eddy simulations are very complicated turbulence models, where the time-dependent flow equations are solved for mean flow and largest eddies (large scale structure), and the effects of smaller eddies (subgrid scale, SGS) are modelled with SGS models. However, large-eddy simulations are at present at developing stage, and the computations are still too costly for general purpose applications.

It is also worthwhile to know that there are other ways to solve the turbulent flow systems without using any turbulence models, so called direct numerical simulation (DNS). DNS directly solves the time-dependent Navier-stokes equations without any need for even a subgrid-scale (SGS) model, and can describe the fluid turbulence much more accurately. However, the use of these methods requires enormous computing time and is not yet widely utilized in engineering applications.

A lot of publications are available on turbulence physics and turbulence modelling. Here are a few of them, and the interested readers can study more if needed: Rodi [430], Markatos [431], Bradshaw [432].

$k - \epsilon$ model and its modifications In this course, we will give some detailed description for just one turbulence model: the standard $k - \epsilon$ model for illustration purpose. The standard $k - \epsilon$ model has been widely used to represent turbulence in many engineering flow simulations. The $k - \epsilon$ model was first proposed by Harlow and Nakayama [433] and was modified by Jones and Launder [434, 435] to account for low Reynolds-number effect near walls. In this model, two additional variables, namely the turbulent kinetic energy k and its dissipation rate ϵ are solved to determine the turbulent viscosity. The k and ϵ are solved with their own PDEs, where the dissipation rate is defined as $\epsilon = k^{3/2}/l_m$ to give the definition of the mixing length l_m. The transport equations for k and ϵ can be obtained from the Navier-Stokes equations by a sequence of algebraic manipulations. For incompressible flows, the well-known two equations for the turbulent kinetic energy and the viscous dissipation rate of the $k - \epsilon$ model can be expressed as follows.

$$\frac{\delta(\rho k)}{\delta t} + \frac{\delta(\rho \overline{u}_j k)}{\delta x_j} = \frac{\delta}{\delta x_i}\left(\frac{\mu_t}{\sigma_k}\frac{\delta k}{\delta x_j}\right) + G_k - \rho\epsilon \tag{A.102}$$

$$\frac{\delta(\rho\epsilon)}{\delta t} + \frac{\delta(\rho \overline{u}_j \epsilon)}{\delta x_j} = \frac{\delta}{\delta x_j}\left(\frac{\mu_t}{\sigma_\epsilon}\frac{\delta \epsilon}{\delta x_j}\right) + \frac{\epsilon}{k}(C_{1\epsilon}G_k - \rho C_{2\epsilon}\epsilon) \tag{A.103}$$

where, G_k is the production rate of turbulent kinetic energy k and is described as follows:

$$G_k = -\overline{\rho u_i' u_j'}\frac{\delta u_i}{\delta x_j} \approx \mu_t\left(\frac{\delta u_i}{\delta x_j} + \frac{\delta u_j}{\delta x_i}\right)\frac{\delta u_i}{\delta x_j} \tag{A.104}$$

The empirical parameters commonly used in the $k - \epsilon$ models are: $C\mu$=0.09, $C\epsilon_1$=1.44, $C\epsilon_2$=1.92, σ_k=1.0, and σ_ϵ=1.3. The $k - \epsilon$ model has been combined with compressible Navier-Stokes equations with additional compressible terms. However, these added terms were usually found insignificant up to a Mach number of five, and are frequently dropped. For heat transfer with strong buoyancy effect, additional terms are required.

The $k - \epsilon$ turbulence model has been widely used in modelling most engineering applications. It usually gives fairly reasonable results compared to experimental data, although it has several disadvantages in predicting many specific flow situations. The standard $k - \epsilon$ model was also the most frequently implemented turbulence model in commercial general-purpose CFD packages. Due to its isotropic nature and its predictivity for only high Reynolds number flow, the standard $k - \epsilon$ model has had many modifications. Either the model constants are modified to suit different applications, or additional equations or terms are added to overcome the shortcomings of the standard $k - \epsilon$ model. For instance, the Lam-Bremhorst low Reynolds-number modification of the $k - \epsilon$ model [436] implemented in PHOENICS is to enhance the prediction of separation or laminarisation. A $k - \epsilon$ model based on the Renormalization Group (RNG) theory, the RNG-$k - \epsilon$ model [437], is another example of modifications. The standard $k - \epsilon$ model is known to be too dissipative; the turbulent viscosity in recirculations tends to be too high, and thus damps out vortices. The RNG-$k - \epsilon$ model attempts to correct this fault by using slightly different constants, and by adding an extra source term to the ϵ equation.

When simulating turbulent flows using a turbulence model, it is always a challenging task to model the viscosity-affected near-wall regions. At wall boundaries, both wall-functions and low Reynolds-number approaches can be applied. The wall-function method is a traditional approach to resolving the flow problems of the near-wall regions. The well-known law-of-the-wall approach has been the technique most commonly adopted in the applied CFD fields. In the wall function approach, the viscous sub-layer is bridged by employing empirical formulas to provide near-wall boundary conditions for the momentum and turbulence transport equations. These formulas connect the wall conditions to the dependent variables at the near-wall grid node lying in fully turbulent fluid. The advantages of wall-function method are that it escapes the need to extend the computations right down to the wall, and that it avoids the need to account for the viscous effects in the turbulence model. The low Reynolds-number method uses a fine-grid analysis, and the computations are extended through the viscosity affected sub-layer close enough to the wall where laminar flow boundary conditions are applied. Various low Reynolds-number $k-\epsilon$ turbulence models are available. However, the disadvantage of the low Reynolds-number method is that a fine grid is still required in each near-wall region.

Modelling of multi-phase flow

Multi-phase flow is another issue for industrial process simulation, which include gas-solid, gas-liquid, and gas-solid-liquid systems. In modelling the multi-phase flow systems, three major groups of models are available. The first one is the Eulerian - Eulerian approach, or so called the two fluid model [438]. It treats both phases as interpenetrating continuous media. The second one is the Eulerian - Lagrangian approach [438], which treats the carrier fluid as the continuous phase, and the dispersed phase in the moving Lagrangian frame with Newton's second law. The third one is the free-surface flow modelling. Nowadays, most of the commercial CFD packages have capabilities to model all three types of multi-phase flow systems with different levels of complexity. In this short course, we will not deal with the multi-phase flow systems, however, this issue will be addressed in the following as a general knowledge. The interested reader can get more information from literature.

Eulerian - Eulerian two-phase flow In the Eulerian - Eulerian approach, the interpenetrating phases may have different velocities, temperatures, but they usually share a common pressure. These intermingling phases may exchange mass, momentum as well as enthalpy. The share of the space of each phase is treated as volume fraction, and it is a function of location and time. All the phases together fill completely the space available. In Eulerian - Eulerian models, the governing equations of the different phases are basically the Navier-Stokes equations. Each phase occupies only a part of the space indicated by its volume fraction, and the phases are allowed to exchange mass and other properties.

The equations for the volume fractions ri are expressed as follows:

$$\frac{\delta(\rho_i r_i)}{\delta t} - div(\rho_i r_i \mathbf{u}_i) - div(\Gamma_r \, grad \, r_i) = m_{ji} \tag{A.105}$$

transient term + convention term - diffusion term = source term

For other properties ϕ_i of phase i, the conservation equations can be written in a generalised form as follows:

$$\begin{aligned}\frac{\delta(\rho_i r_i \phi_i)}{\delta t} &+ div(\rho_i r_i \phi_i \mathbf{u}_i) - div(\Gamma_\phi r_i \, grad \, \phi_i) = S_{\phi i} \\ &+ (f_{ij} + [m_{ji}])(\phi_j - \phi_i)\end{aligned} \tag{A.106}$$

$$\begin{array}{l}\text{transient}\\ \text{term}\end{array} + \begin{array}{l}\text{convention}\\ \text{term}\end{array} - \begin{array}{l}\text{diffusion}\\ \text{term}\end{array} = \begin{array}{l}\text{source}\\ \text{term}\end{array} - \begin{array}{l}\text{interphase}\\ \text{transport term}\end{array}$$

where the property variable ϕ can be a velocity component for momentum equation, enthalpy or temperature for thermal energy equation, or mass fraction for species equation. In Equations A.105 and A.106, the symbols used have the following meaning:

ρ_i	is the density of phase i
V_i	is the velocity of phase i
Γ_r	is the diffusion coefficient
m_{ji}	is the interphase mass transfer rate from phase j to phase i;
Γ_ϕ	is an exchange coefficient
$S_{\phi i}$	is a source term (e.g. pressure gradient $-r_i\frac{\delta p}{\delta x}$, $-r_i\frac{\delta p}{\delta x}$, $-r_i\frac{\delta p}{\delta z}$, if ϕ is a velocity component)
f_{ij}	is the interphase friction (e.g. drag)
$[m_{ji}]$	indicates the maximum of 0 and m_{ji}

In addition to Equations A.105 and A.106, the system must satisfy the closure equation for volume fraction:

$$\sum r_i = 1 \tag{A.107}$$

Various physical formulas are available for the inter-phase drag coefficient, which covers most of the applications. An example is the drag coefficient in a gas phase as suggested by Clift et al. [439]:

$$C_d = \frac{24.0}{Re}(1.0 + 0.15Re^{0.687}) + \frac{0.42}{1.0 + 4.25 \cdot 10^4 Re^{-1.16}} \tag{A.108}$$

It can be seen that the drag coefficient is dependent on the particle Reynolds number based on the slip velocity V_{slip} and the particle diameter D_p and the kinematic viscosity of the gas phase: $Re = \frac{V_{slip}D_p}{v_g}$. The Eulerian - Eulerian approach is more appropriate when the particle loading is high than the the Eulerian - Lagrangian approach which is better for dilute loading conditions. However, both approaches have their merits in certain aspects of particle flow behaviour. In PHOENICS, the Eulerian - Eulerian two phase equations are solved with Inter-Phase Slip Algorithm - IPSA [440], which is the multi-phase counterpart of SIMPLEST for single phase flows. The IPSA solution cycle works in a similar way as the SIMPLEST cycle. The main feature is the way in which the pressure-correction equation is constructed, and this corresponds to the SIMPLEST algorithm used in the single-phase flows of PHOENICS.

Eulerian - Lagrangian two-phase flow Unlike Eulerian - Eulerian models, Eulerian - Lagrangian models do not regard both phases as interpenetrating continua. Instead, they model one of the phase (the "carrier phase") as a continuum, and the others (the "dispersed phases") as particulate ones which travel across the continuous phase. Eulerian - Lagrangian models represent the continuous phase through Eulerian equations, similar to those used for single-phase flows and to those for Eulerian - Eulerian models. However, Lagrangian equations are used for the dispersed phases. These equations track the particles as they move through the continuous phase, exchanging mass, momentum and other properties.

For the carrier phase, the generalised Eulerian equation is expressed as follows:

$$\frac{\delta(\rho\phi)}{\delta t} + div(\rho\phi\mathbf{u}) - div(\Gamma_\phi \; grad \; \phi) = S_\phi + S_{particles} \tag{A.109}$$

transient term + convention term - diffusion term − source term + source term from particles

The Lagrangian equations are used for tracking particle phase, which can be integrated to give particle position, velocity, size, temperature etc. as a function of time. The equations are typically expressed as follows:

- **Particle trajectory**:
$$\frac{dx_p}{dt} = \mathbf{u}_p \tag{A.110}$$
- **Particle momentum**:
$$\frac{d(m_p\mathbf{u}_p)}{dt} = D_p(\mathbf{u} - \mathbf{u}_p) - m_p\left(1 - \frac{\rho}{\rho_p}\right)\mathbf{g} - V_p \; grad \; p \tag{A.111}$$
where D_p is the drag function: $D_p = \frac{1}{2}\rho A_p C_d|\mathbf{u} - \mathbf{u}_p|$, V_p is the particle volume, $grad\,p$ is the continuous phase pressure gradient. A_p is the particle projected area, and C_d is the drag coefficient which can be expressed the same as in Equation A.108.
- **Particle enthalpy**: for heat exchanging, melting/solidifying and vaporising particles
$$m_p C_p \frac{dT_p}{dt} = m_p L \frac{df_s}{dt} + H\frac{dm_p}{dt} + \alpha(T_g - T_p) \tag{A.112}$$
Where C_p is the specific heat of the particle, L is the latent heat of solidification, H is the latent heat of evaporation, f_s is the proportion of the solid phase in the particle (solid fraction). α is the heat transfer coefficient between the particle and the surrounding fluid, and T_g and T_p are the temperatures of the surrounding fluid and particles, respectively.
- **Particle mass**: for vaporising particles
$$\frac{dm_p}{dt} = -\pi d_p \frac{k_v}{C_{pv}} Nu \cdot \ln(1 - B_M) \tag{A.113}$$
where d_p is the particle diameter, k_v is the thermal conductivity of the vapor from the evaporation of the particle or droplet, C_{pv} is the specific heat of the vapor, Nu is the Nusselt number determined by particle Reynolds number (Re) and Prandtl number (Pr) of the continuous phase, $Nu = 2(1 + 0.3Re^{0.5}Pr^{0.33})F$, F is the Frossling correction factor for mass transfer ($F = \frac{\ln(1 - B_M)}{B_M}$), and B_M is the mass transfer number representing the driving force in the mass transfer process.

The above ordinary differential equations for particles are simple in form, and their integration is straightforward if the continuous phase field is known. However, the equations of the particle phase are coupled with the continuous phase through the inter-phase exchange terms (e.g. drag, temperature, droplet vaporisation, etc.), and the equations of continuous phase are also coupled with the particle phase through particle source term. For this reason, the solution procedure has to iterate between the solution algorithms for both phases. The well-known procedure PSI-Cell (Particle Source-In Cell, proposed by Crowe et al. [441]) is normally used to the solutions. After the solution, particle trajectories and particle history (diameter, position, temperature, velocity etc.) as function of time are obtained and can be plotted in the post-processing stage of the modelling. In PHOENICS, Lagrangian particle tracking is done through a module called GENTRA, the general particle tracker. There have been a lot of discussions on which approach is better: Eulerian or Lagrangian for the dispersed phase [442, 443]. A comprehensive literature survey is good for a general reading [444].

Free-surface flows Free-surface flows involve the interaction of two or more distinctly different fluids, separated by sharply defined interfaces. The position of the interface is not known a priori. Many metallurgical processes (ferrous and nonferrous) are involved with free-surface flows. Examples are flows of molten slag, metal or matte in smelting or refining furnaces in contact with gases above, and in many cases there are gas injections into the melt, either through bottom tuyeres or from a top lance (submerged or non-submerged) in furnaces. Typical examples are gas injection to ladles, mould filling, continuous casting operations. In theses processes, the free-surfaces are either in the bubble-liquid interfaces, or the bulk melt-gas phase interface, or quite often liquid-liquid-gas interfaces as in gas-slag-matte (and/or metal) systems. It may involve gas-bubble formation, growing and movement in the liquid bath, or the surface swelling and wave motion. Other free-surface phenomena can be found in tank sloshing and tank rupture. Although modelling the free-surface flows is a very difficult task, different methods have been developed to model different aspects of free-surface flows. The mathematical model will need to locate the unknown inter-fluid boundaries, at which discontinuities exists in one or more flow quantities; to satisfy the field equations governing conservation of mass, momentum, energy etc.; and to be consistent with boundary conditions. The following methods are commonly used in modelling the free-surface flows:

- Scalar Equation Method (SEM)
- Height of Liquid Method (HOL)
- Volume of Fluid Method (VOF)

The Scalar Equation Method (SEM) deduces the interface position from the solution of the conservation equation for a scalar "fluid marker" variable [445]. The local physical properties such as density and viscosity are set to those of appropriate fluid according to the value of the scalar marker variable. This method is used for example in PHOENICS. It should be noted that SEM is for transient case only, and the surface tension is not taken into account, and the method is prone to numerical diffusion (non-realistic diffusion).

In the Height of Liquid Method (HOL), the location of the interface is determined from the solution of liquid balance equations, by calculating the volume fraction of liquid in every cell. HOL method can handle both steady and transient cases, and does not generate numerical diffusion. However, HOL method cannot cope with "overturning" motions of fluid, or the situation with inter-connected regions of open spaces and solid blocks. HOL is used in PHOENICS as one of the free-surface flow options.

The Volume of Fluid Method (VOF) simulates two or more immiscible fluid phases, in which the position of the interface between the fluids is of interest [446, 447]. In the VOF method, a single set of momentum equations is shared by the fluids, and the volume fraction of each fluids is tracked throughout the domain. The effects of surface tension, wall adhesion angle, heat transfer from walls to each phases and between phases can be included in the model. The tracking of interface(s) between the phases is accomplished by the solution of a continuity equation for the volume fraction of one or more of the phases. The properties in the transport equations (e.g. density, viscosity, thermal conductivity) are determined by the presence of the component phases in each control volume. Application of the VOF method include the prediction of jet break-up, the motion of large bubble in a liquid, the motion of liquid after a dam break, or the steady or transient tracking of liquid-gas interface. FLUENT, FIDAP and FLOW-3D are supplied with VOF model for free-surface modelling.

Modelling of radiative heat transfer

Thermal radiation is an important mode of heat transfer at high temperatures in most engineering combustion systems. This mode of heat transfer differs from convection and conduction in such a way that in addition to the dependence on three space coordinates, it also depends on the space angle and wavelength. There are two types of radiation problems in engineering, depending on whether or not the fluid media participate in the radiative heat transfer processes.

- **Surface-to-surface radiation:** First type of radiation problems deals with radiation between surfaces separated by a medium which does not absorb or emit radiation. This situation applies to the systems under vacuum or the intervening medium is composed of monoatomic or symmetrical diatomic gases such as N_2, O_2 or H_2. We called this type of radiation problems as radiation between surfaces in transparent (non-participating) media. The radiant interchange between the surfaces requires determination of matrices of corresponding geometric view factors or alternatively the radiative exchange factors, and the approach is different from that for radiative heat transfer in participating media. Examples of incorporating surface to surface radiation in CFD packages can be found in PHOENICS. Surface-to-surface radiation model (STSR) in PHOENICS is essentially a zonal method, in which the surfaces participating in the radiative exchange process are sub-divided into a number of isothermal zones. In the solution of the energy equation, the model allows for radiative exchange between the surfaces via the imposition of a heat balance at each thermal zone. Essentially, the view factors (for black body) and radiative exchange factors (for grey body) for the enclosures (3-dimensional) have to be supplied by the users. In addition to PHOENICS, FIDAP also provides possibility for surface-to-surface radiation modelling. Details about surface to surface radiation will not be discussed in this report, since its less importance in metallurgical processes. The interested readers can refer the book by Szekely and Themelis [427].
- **Radiation in participating media:** When the radiation enclosure contains more complex molecules such as CO_2, H_2O, NH_3, SO_2, or fine solid particles, as in the case of luminous flames or particulate suspensions in a chemical or metallurgical reactor, the furnace atmosphere participates in the radiation process. We call this kind of media as participating media, which are non-transparent to radiation. Different approach has to be used in the treatment. The radiative heat transfer in participating media is described by the radiative transfer equation (RTE). RTE forms the basis for describing the transfer of radiant energy in an absorbing-emitting-scattering medium. This equation is an

> integro-differential equation, and because of this it is very difficult to solve exactly for multi-dimensional geometries. In addition, the general problem is complicated further by the need to account for the spectral variation of the radiative properties of the various materials (gases, surfaces, particles). This report introduces some aspects for modelling radiative heat transfer to obtain certain levels of solutions to the RTE.

Most workers have sought to simplify the RTE by making certain simplifying assumptions, such as those concerning the discretisation of angle and wavelength. For example, the wavelength and angle dimensions of radiation can be discretised by sub-dividing the former into discrete wave bands and the latter into discrete angles represented by fluxes. The simplifying assumptions that are finally adopted depend on a number of factors: the nature of the application, the degree of accuracy required, the characteristics of the medium, and the available computer facilities. Consequently, many different radiative transfer models have been developed over the years, such as Zonal method, Monte Carlo method, Flux method, Discrete transfer method, etc. [448, 449, 450].

Radiative Transfer Equation (RTE) Radiative heat transfer in non-transparent media is governed by the general Radiative Transfer Equation (RTE) of the radiation intensity of the media, expressed in the differential and integral form:

$$\frac{dI}{dl} = -(K_a + K_s) \cdot I + K_a I_b(T) + \frac{K_s}{4\pi} \int_{4\pi} p(\theta) I(\Omega) d\Omega \tag{A.114}$$

$$\begin{array}{c}\text{Intensity}\\ \text{variation}\end{array} - \text{Attenuation} + \begin{array}{c}\text{Local}\\ \text{emission}\end{array} + \text{In-scattering}$$

This represents the intensity variation of a beam through a differential element of length dl. The right hand side of Eq. A.114 consists of the attenuation term of the beam by absorption and out-scattering, the augmentation contributed by the local thermal emission, and the intensity increase due to scattering into the reference beam from radiation incident on the differential element throughout 4π steradians. In the RTE, I_b is the total intensity associated with the blackbody emissive power at local temperature ($I_b = E_b/p = \sigma T^4/p$). K_a and K_s are the absorption and scattering coefficients of the media. $p(\theta)$ is the phase function for in-scattering. The last integral term is the most difficult task for solving the RTE. For isotropic scattering, the value of the phase function becomes unity. For anisotropic scattering, the phase function $p(\theta)$ should be calculated from the characteristics of each particle for each photon separately.

Obtaining the temperature field is the final aim of the computation task concerning the heat transfer. Due to the coupling of the radiation energy with the temperature field, the radiation term is treated as a source-sink term S_r in a total energy equation, with the rate of volumetric net absorption of radiation:

$$S_r = K_a \int_0^{\infty} \int_{4\pi} [I_\lambda(\Omega) \quad I_{b\lambda}] d\Omega d\lambda \tag{A.115}$$

where, $I_\lambda(\Omega)$ is determined by the previous RTE A.114. The determination of the source-sink term involves the integration over all wavelengths and throughout 4π steradians. Thus it is a triple integration altogether, and is a very complicated task to solve at all grid points in a finite difference simulation. Therefore, simplification of both the RTE and the source-sink term expression forms the different radiative heat transfer models. In this course, only the composite flux model will be introduced. For other models, good reference can be found for details.

The composite flux model Among many different radiation models, the flux models in which radiation intensity balances are set up for flow along the coordinate grid are better suited for use with the finite difference solutions of the flow equations. The composite-flux model of Spalding [451] is one of the radiation models in PHOENICS for participating gray media. In the composite-flux model, the radiation fluxes can be written in the second order PDEs, which have the form of a diffusion equation, e.g. for X-coordinate flux R_x defined as $R_x = 1/2(I_x^+ + I_x^-)$:

$$\frac{\delta}{\delta x}\left(\frac{1}{K_a + K_s}\cdot\frac{\delta R_x}{\delta x}\right) = \left(K_a + \frac{2}{3}K_s\right)R_x - K_aE_b - \frac{K_s}{3}(R_y + R_z) \tag{A.116}$$

The terms on the right-hand side of Equation A.116 are treated as source terms for the radiation fluxes in the diffusion equation. The enthalpy source to the gas phase is the difference between the absorbed energy and the emitted energy, expressed as follows:

$$S_r = 2K_a(R_x + R_y + R_z) - 6K_a\sigma T^4 \tag{A.117}$$

In the composite-flux radiation model, the emitting, absorbing and isotropic scattering of the media are taken into account. However, non-isotropic scattering is not included. In the calculation, the wall boundary conditions or the radiation exchange with the media have to be considered. A Cartesian form of the six-flux model associated with its implementation in PHOENICS was described by Hoffmann and Markatos [452]. The success of flux methods depends on how well the intensity distribution is represented by the intensities along the coordinate axes. Three coefficients are needed in this model computation, which will be discussed later in more detail:

- absorption coefficient of the media: K_a,
- scattering coefficient of the media: K_s, and
- wall emissivity: ϵ_{wall}.

Radiative properties of the medium [453] In general the radiative properties of the medium vary with the local composition and wavelength. The products of combustion, such as CO_2 and H_2O, or SO_2 in the off-gases of sulphide smelting processes, are strong selective adsorbers and emitters of radiant energy, but do not scatter radiation significantly. Particulates, such as pulverised coal, ash and soot, concentrate particles or flue dust, strongly determine the scattering, as well as absorbing and emitting radiation. However, the radiation attenuation of N_2, O_2 and H_2 is so small that these gases are almost completely transparent to radiation. However, a detailed modelling of the radiative properties is not warranted for the differential radiation models considered here. Rather these models require specification of the mean absorption coefficient K_a and the mean scattering coefficient K_s, which may be interpreted as 'gray' values that are representative of the entire spectrum. It should be noted that the absorption coefficient K_a is not to be confused with the conventional coefficient which appears in the RTE. The specification of these coefficients has been discussed in some detail by Gosman and Lockwood [454], although many workers simply use constant values or values dependent only on the local composition. For example, Hoffmann and Markatos [452] used $K_a = 0.1m^{-1}$ and $K_s = 0.01m^{-1}$ for hydrocarbon combustion. Another approach is to use the "mixed gray and clear" gas formulation of Hottel and Sarofim [455] to determine the total gas emissivity egas. The value of the absorption coefficient K_a is then obtained from the "psuedo-gray" approximation

$$\epsilon_{gas} = 1 - \exp(-K_a \cdot L) \qquad \text{(A.118)}$$

and

$$K_a = \frac{-\ln(1 - \epsilon_{gas})}{L} \qquad \text{(A.119)}$$

where L is a characteristic path length for a cell. In general this method implies that K_a varies from cell to cell as a function of L, temperature and composition. However, the method may be used to estimate a representative constant value of K_a. With a mean beam length L_m and a mean gas emissivity in a temperature range. L_m can be related to the total volume of the geometry (V) and total surface area (A) in the geometry experiencing radiative heat transfer: $L_m = 3.6V/A$. Further details can be found in the following references: Abbas et al [456], Siegel and Howell [457] and Viskanta and Mengüç [450]. If scattering is relatively unimportant, the coefficient K_s can be set to a relatively small value, say $0.1 \times K_a$. Otherwise, larger values of K_s are required, as for example when particulates are present.

In practical computations, constant values of K_a and K_s are usually assumed, although they are dependent on the temperature and compositions of the media. The wall emissivity can be set to different values in different wall areas. K_a and K_s from gas-phase and particles are determined according to the gas compositions and dust loading, and the geometry of the flow domain in the average temperature range.

Other radiation models Flux models are the simplest radiation models, with their merits for the computational economy. However, there are many other radiation models, which have been developed in the past, and some of them have been incorporated in various CFD packages. The following is a brief list about different radiation models, and it is meant only to guide the interested readers for further studies: (1) Zonal method; (2) Monte Carlo method; (3) Flux method: Six-flux model (as described in the composite flux model); spherical harmonics method (P-N method); discrete-ordinate method; (4) Discrete transfer method. About the details of different radiation models, one can refer to several comprehensive papers by Howell [448], Sarofim [449] and Viskanta and Mengüç [450].

A.3.3 Examples of the modelling of furnaces

In this section two examples by the authors are shown to demonstrate the use of CFD in the waste and recycling fields. This work is of fundamental importance to understand the link between material feed quality and furnace performance and optimization. As stated by Reuter [33], if furnaces can be optimized, they play a key role in minimizing losses and closing the material cycle and hence making Industrial Ecology happen

Submerged arc phosphorous furnace model

A submerged arc furnace is a very complex system in both physical and chemical aspects. It involves multi-phase, high temperature reduction reactions, energy conversion and distribution from electric power through arcs and conduction. The reduction rate, product recovery and energy consumption are a few primary concerns for the production. Up to now, many of the interrelated physical, chemical and dynamic aspects are still not very well understood.

Submerged arc furnaces have the interesting property that the electrical side of the furnace can be controlled rather well, but that one cannot characterise the particulate feed or define the distributed properties of the process very accurately. In order to be able to best control these furnaces one has to combine electrical and metallurgical aspects in such a way that both aspects are taken care of in the most optimal way. Whereas time constants allow the electrical side to be well controlled in a feedback way, it is owing to larger, distributed residence times of material and its changing properties in the furnace, that the metallurgy can only really be controlled effectively in a feedforward way.

In any search for supplementary feedforward, predictive submerged arc furnace control it soon becomes apparent that it is very difficult to create sufficiently accurate and practically useful predictive, dynamic, first principle metallurgical models. Although an improvement in predictive accuracy will most certainly come about with more frequent analyses of feed and product characteristics, it is a fact of life that certain practical and financial constraints inside a company often prevent such measures.

One proven approach is to develop dynamic transfer function models based on reconciled plant data, as well as simplistic, yet representative thermodynamic equilibrium prediction models with the help of artificial intelligence techniques. This method resulted in equilibrium autoregressive moving average models with exogenous variables (Equilib-ARMAX) successfully tested on bath type furnace process data. With a phosphorus producing submerged arc furnace, however, it becomes increasingly difficult for standard thermodynamic and kinetic modeling (as well as the associated software) to provide adequate decision support for the predictive dynamic model. Heterogeneously distributed properties diminish thermodynamic influence on prediction and its capacity to assist in feedforward control.

A big and ongoing challenge, therefore, lies in exploiting the thoroughly accurate and readily available electrical knowledge in such a way as to cast a predictive light on the kinetic path of the process between tap events. It will be shown that such a venture not only encapsulates significant 3-dimensional aspects of the furnace in the predictive model, but provides much needed assistance in understanding of the furnace.

Figure A.19 shows the considerable advances have been made in the simulation of an industrial 60MW thermal phosphorous SAF in south of The Netherlands [458]. The interesting aspect of this work is that in addition to processing primary mineral ores, these furnaces also process recycled phosphorous materials (e.g water purification sludges, animal and other organic wastes, etc.), complicating the furnace operation considerably, making fundamental studies and process control models imperative. It is the objective to include CFD models into already developed dynamic control models by the authors for predicting slag quality, MWh/t etc. This reactor demonstrates the innovative use high temperature technology and the use of fundamental approaches to close the P-material cycle, a typical recycling scenario, that requires considerable fundamental study to solve!

To study these aspects a process model was developed by using a combination of dynamic modelling and CFD techniques. The process is the large-scale production of phosphorus using the Wohler process. The main reaction proceeds according to Equation A.120, producing a calcium-silicate slag, calcium fluoride, carbon monoxide and the desired product, phosphorus gas.

$$\begin{aligned} &\mathrm{Ca_{10}(PO_4)F_2 + 15C + 9_z SiO_2 \rightarrow 3P_2(g)} \\ &\mathrm{+ 9[(CaO \cdot SiO_2)_z] + CaF_2 + 15CO(g)} \end{aligned} \tag{A.120}$$

Considerable work has been done to model submerged arc furnaces on the basis of CFD. Various depth of knowledge is available for these furnaces from various data measured by the authors, included plant experience, thermodynamic slag models developed by the authors as well as kinetic data measured for direct reduction in the plant's ores.

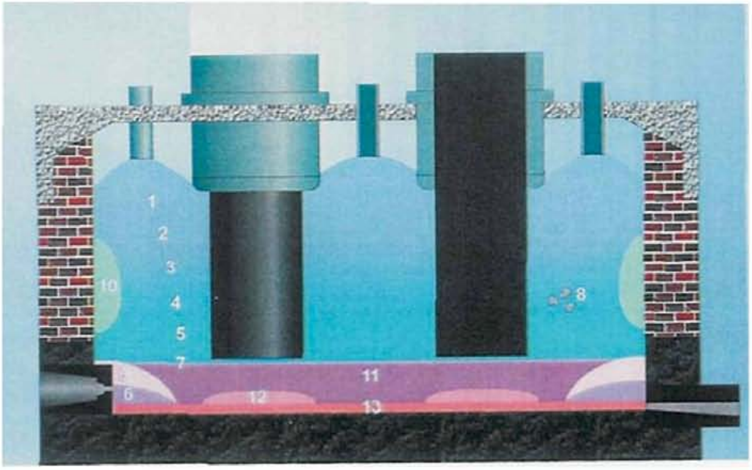


Figure A.19: Phosphorus producing sub-merged arc furnace. The slag tap holes are situated on the left and the ferrophosphorus tap hole on the right of the figure.

To construct a CFD model, detailed process data are required. Therefore, a real industrial furnace for phosphorus production was used as the main reference to deduce and define the furnace dimensions, productivity and boundary conditions. Some of the basic furnace dimensions and major operating conditions for the current model are listed in Table A.13. All production data are calculated based on an average time step (time between sampling of feed and product streams) of 9 hours.

A general purpose CFD code, Fluent 6.1, was used to generate the basic furnace model depicted by Figure A.20. The model is fully 3-dimensional, including 3 electrodes, a ferrophosphorous layer, a slag layer, a solid burden layer and open space between the ceiling and solid feed. The solid burden zone has been subdivided into separate zones. Three small reaction zones were created underneath the electrodes, while the remaining burden zone was divided

Table A.13: Furnace dimensions and major operating conditions for the current process model

Items	Details
Dimensions	
Long-end furnace inside diameter (mm)	
Carbon lining wall thickness (mm)	
Outside height of the furnace (mm)	
Electrode diameter (mm)	
Electrode operating depth (mm)	
Pitch circle diameter (mm)	
Thickness of ferrophosphorus layer (mm)	50
Thickness of slag layer (mm)	450
Thickness of solid burden zone (mm)	3400
Outlet diameter (mm)	
Production Data	
Diameter of reaction zones	2000
Gaseous production rate (ton/time step)	102
Slag temperature (Kelvin)	Generated
Ferrophosphorus temperature (K)	Generated
Energy consumption (MW)	≈ 40

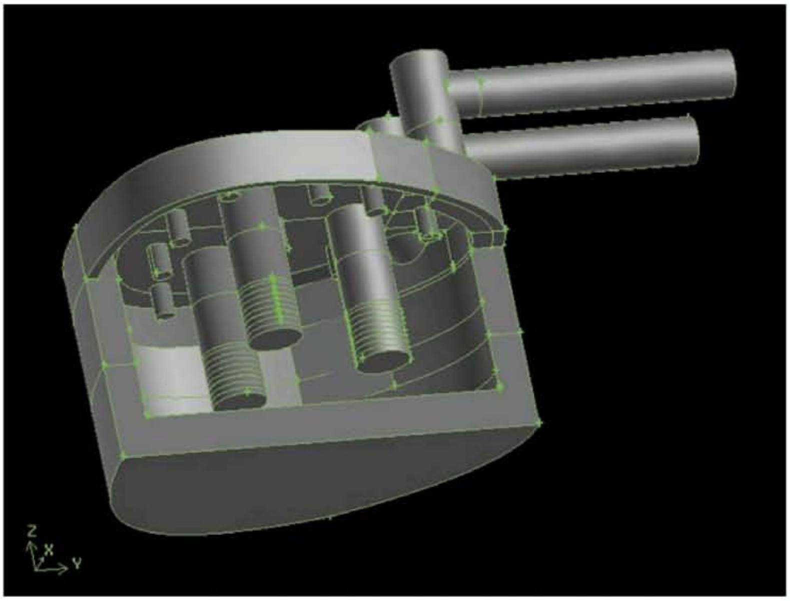


Figure A.20: Graphical representation of a 60MW closed submerged arc furnace for phosphorus (P) production, depicting the furnace wall, the three electrodes (three phase) and the closed two offgas pipes for recovering the P-CO gas mixture

into an upper and lower part. This enables the user to define different porosities. In the current model, one gas stream (CO and P_4 mixture) was simulated. Solid feed only provide resistance to gas flow. Electrical and arc heating were taken as volumetric heat sources, all generated from the above-mentioned three reaction zones. The influence of an electromagnetic field on the gas flow has initially been neglected. Available experimental data were utilised to construct a neural network model (Microsoft Excel) that allows the gas mass flow generated to be solved as a function of temperature in the burden, residence time at required temperature and type of ore utilised. To obtain effective energy dispersion (arc and Joule heating), a higher thermal conductivity value for the gas was used to simulate the electrical heating, before the real arcs and Joule heating were modelled. For the furnace geometry, both the inner geometry and actual walls thicknesses with their manufacture specifications were used. The outer wall was set at a constant temperature of 27°C. CO and P_4 gas flow was modelled with the standard k-ϵ turbulence model, and the flow resistance was coded with Ergun's equation by assuming a constant bed porosity of 0.37 in the burden. The Discrete Transfer Radiation Model from Fluent was used to simulate radiative heat transfer. Figure A.20 shows the basic furnace structure generated for the CFD solver.

Figure A.21 shows the predicted temperature distribution in the burden through a cross section view of the furnace. The maximum gas temperature could be as high as 2450°C below the electrodes in the reaction zones and in the outlet ducts a temperatures between 500-700°C are predicted. Clearly, a large temperature gradient in the packed bed is observed.

Figure A.22 shows the predicted gas velocity vectors inside the furnace. At the upper part of the furnace, the gas flows around the electrodes and bends towards the outlet ducts. The outlet duct were lengthened beyond their actual size in order to facilitate better solving of

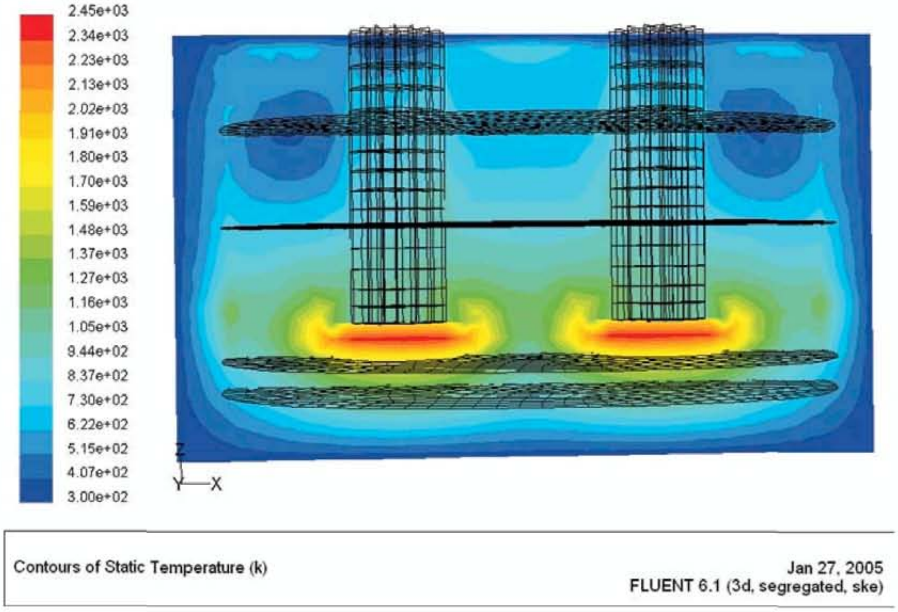


Figure A.21: Temperature profile inside the submerged arc furnace

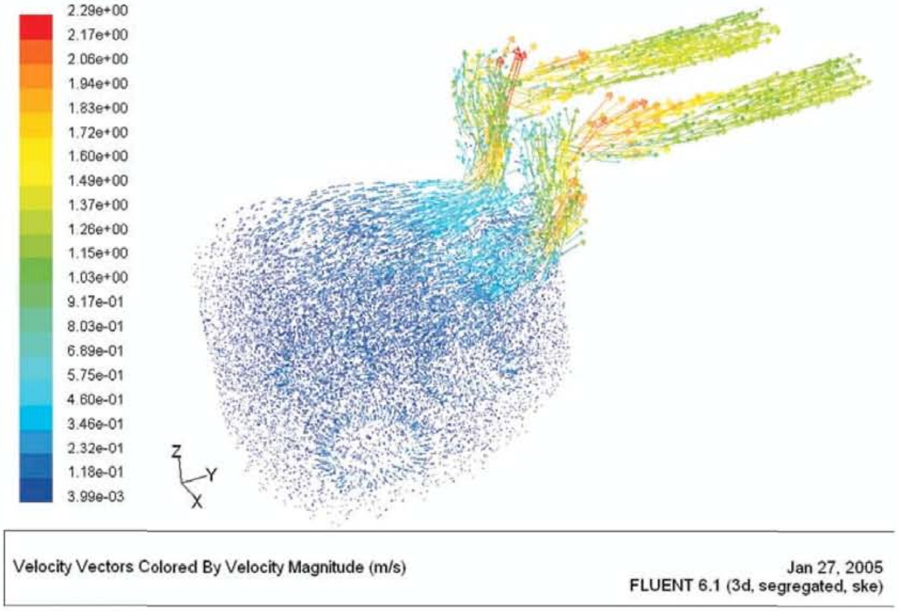


Figure A.22: Gas velocity profile inside the submerged arc furnace

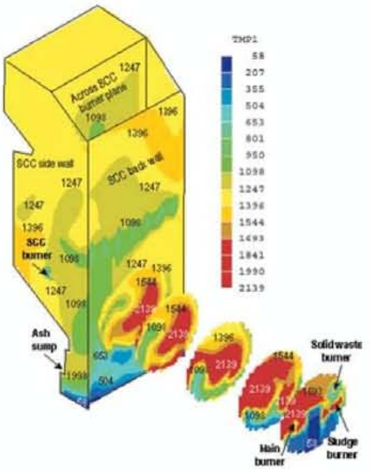


Figure A.23: Temperature profiles in a chemical waste incineration kiln

the coupled equations.

Chemical waste incineration

Thermal waste processing has all the ingredients of pyrometallurgy i.e. high temperature, slag, flue dust, refractories etc. If one considers that high temperature reactors are closers of the material cycle these waste incinerators are extremely important in the material cycle. Also, much of the knowledge assimilated over many years in pyrometallurgy i.e. slag solution chemistry, refractory wear etc., can be used directly in this field. Figures A.23 and A.24 demonstrates the use of CFD in the simulation of the gas flow and temperature in chemical waste incineration kiln to model offgas compositions such as NOx, CO and estimate if dioxins are formed. It is also shown how CFD can be used in the control structure of such a kiln and to train operators. Also the temperature the refractories experience as well as the temperature the slag in the kiln attains can be investigated. These models have been calibrated by plant measurement campaigns [459] [460].

Imperial Smelting Furnace

Not all reactors can simply be modelled by CFD. The Imperial Smelting Furnace is a very complex systems and requires a more pragmatic approach, which includes a combination of thermodynamics and fluid flow, moulded into a more empirical approach applying neural networks . However, the modelled data are all based on the basis presented in Chapters A.2 and A.3.

This furnace plays an extremely important part in closing the zinc and lead material cycle. In order to adaquately control the furnace as a function of constantly changing feed residue and waste materials, is a daunting task. If adaquate furnace control cannot be performed, closing the cycle is really a dream including all philosophical sustainability arguments. In summary, not being able to control furnaces within the constraints of economics and environmental control makes sustainability just a dream. [461]

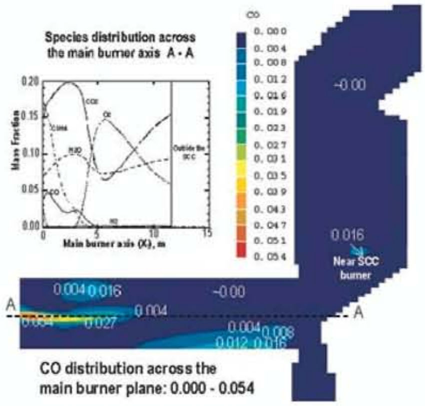


Figure A.24: CO(g) profiles in a chemical waste incineration kiln

Modelling the furnace Figure A.25 gives a schematic overview of the ISF and the connected condenser system. The model describes the shaft furnace and the in- and outputs as depicted on the left side of the figure. The condenser system is not modelled at this stage. Lumpy oxidic material is charged at the top together with lumpy coke. Through the tuyeres, fine coal, oxidic dust and hot air are blown into the shaft. The carbon in the fine coal combusts and carbon dioxide and carbon monoxide are formed. These gasses rise through the shaft reacting with the lumpy feed from the top. In the top part of the furnace the off-gas is collected containing gaseous zinc, carbon monoxide and nitrogen. Hot air is blown in to maintain a constant gas temperature to prevent the zinc vapour from re-oxidation. Liquid lead bullion containing e.g. precious metals is discharged at the bottom of the furnace together with the liquid slag.

The twelve model input parameters described in Table A.14 can be divided into the two groups (i) **(D)**ynamic input parameter group which represent all transfer and fluid flow phenomena, and (ii) **(T)**hermodynamic input parameter group. The dynamic input parameters include the parameters that can be adjusted in the furnace operation any time as desired. To this group belong all furnace inputs; flow rates, compositions and temperatures, many parameters referring to transfer processes as discussed in Chapter A.3. The thermodynamic input parameters are the parameters that are determined by thermodynamic laws as discussed in Chapter A.2. To this group belong all furnace outputs; flow rates, compositions and also temperatures.

The objective of this model is to optimally recover zinc and lead from the feed materials. Modelling the industrial data with CSense 3.3 [462] based on neural networks it is possible to predict the zinc recovery as a function of the variables in Table A.14 with an R^2=0.86. The results are shown in Figure A.26 in which the following can be seen clockwise from top left:

- time series of the zinc production Y (tonnes) with superimposed "Position ruler"
- cause analysis i.e. the parameter(s) that is(are) dominating the output Y at the position of the "Position ruler"
- the expert rule that is currently dominating the process derived from a decision tree analysis of the process data

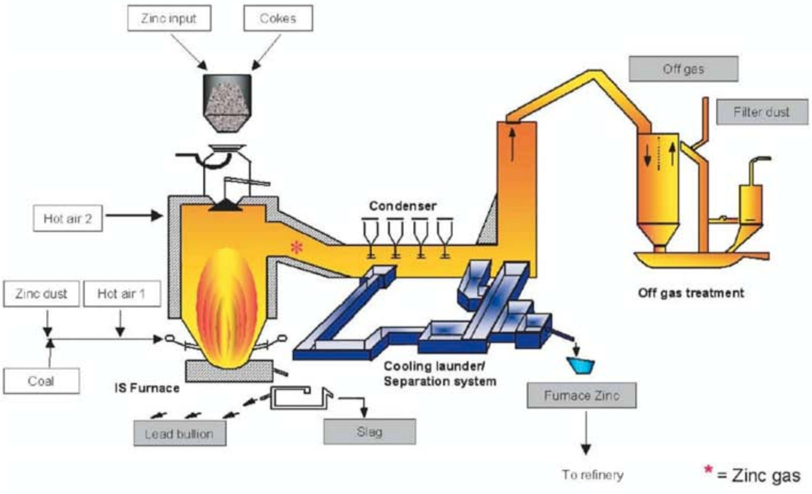


Figure A.25: The Imperial Smelting Furnace (ISF)

Table A.14: Some process variables for the ISF

Model output parameter Y	Model input parameters X_1-X_{12}	Dynamic (D) and Thermodynamic (T)
Y=Zn recovery	X_1=Temperature of blast	D
	X_2=Temperature of cokes	D
	X_3=Hot air 1 flow rate	D
	X_4=Hot air 2 flow rate	D
	X_5=Temperature of slag	T
	X_6=Coke ratio (coke to oxidic input)	D
	X_7=Zinc gas CO/CO_2 ratio	T
	X_8=Sinter structure	D
	X_9=Sinter/Hot briquette ratio	D
	X_{10}=CaO/SiO_2 ratio	D
	X_{11}=Zinc gas flow rate	T
	X_{12}=Lead bullion flow rate	T

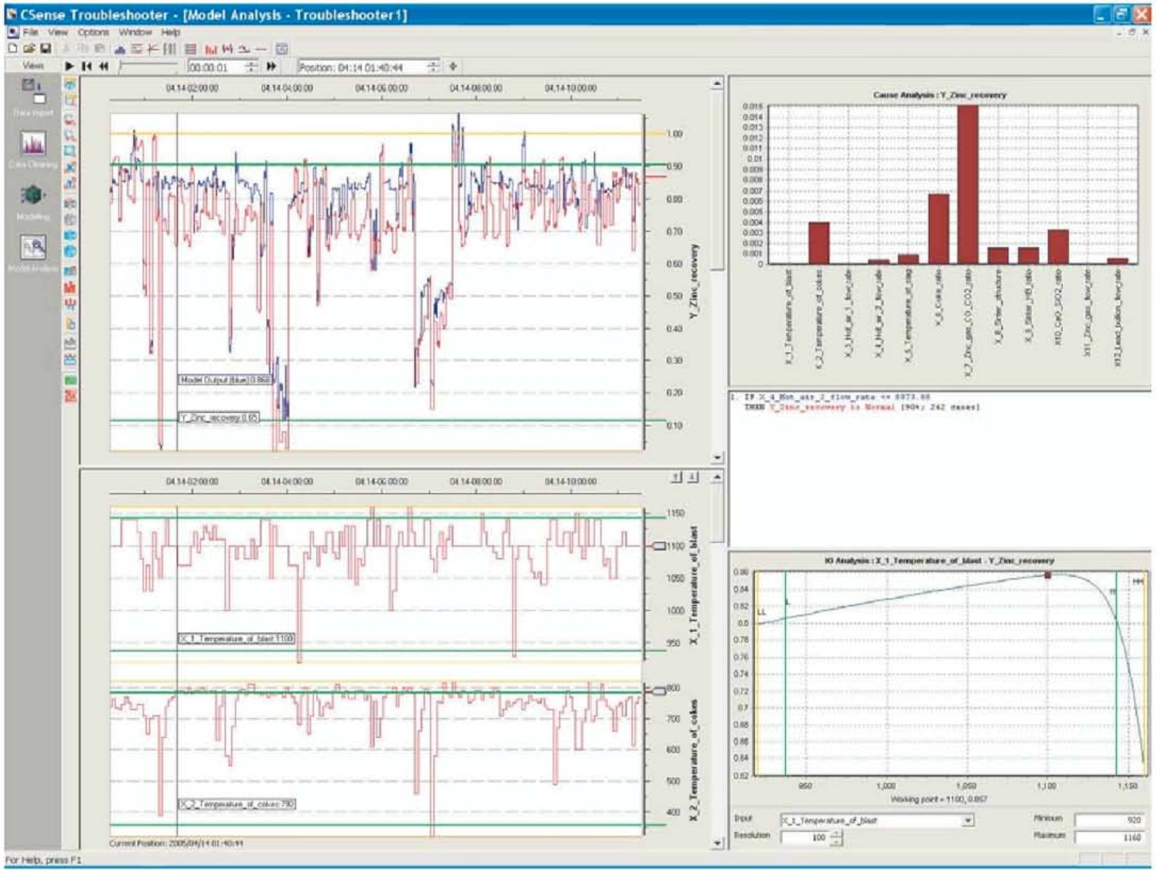
- the two-dimensional relationship between Y and X_1
- time series of X_1 and X_2 associated with Y (scrolling highlights the other variables X_3 to X_{11})

Model results The results indicate that the mode of operation of the furnace jumps between thermodynamic dominated to fluid flow and transfer processes dominated to chaotic in-between operation. In order to obtain valid predictions it is necessary to understand the continuous change between dynamic and thermodynamic regimes in this furnace, because predictions are highly influenced by the interaction between the various parameters in their various states. The model presented here can deal with this and provide good predictions. In addition the model permits troubleshooting and a detailed analysis and cause and effect analysis of each input. This also permits the extremely important analysis of coke usage on zinc production. This has an extreme impact in the case when coke prices are high. From Figure A.26 it is clear that thermodynamics controls the furnace operation i.e. the gas atmosphere CO to CO_2 ratio. For this operating point obviously thermodynamics would adequately describe the furnace.

Moving to another operating point shows that flow phenomena dominate the furnace operation and hence zinc production as depicted by Figure A.27.

In some instances the furnace moves from one operating point to another going into a chaotic mode as depicted by Figure A.28 in which all variables start playing a significant role!

What this example demonstrates is that modelling and controlling industrial furnaces processing recycled materials is by no means easy and can in many cases not modelled simply by using thermodynamics or CFD alone as described in Chapters A.2 and A.3. A more sophisticated combination of models is required which can only be realised if the modeller has a good overview of all modelling techniques and has in-depth theoretical and industrial expertise and knowledge. Without this it is hardly possible to create realistic models for these furnaces and even more difficult to optimise their control. Without these furnace optimally producing metal (in this case zinc) one can hardly speak of closing the cycle or even hence of industrial ecology and hence of sustainability!



```
1. IF X_4_Hot_air_2_flow_rate <= 8973.88
   THEN Y_Zinc_recovery is Normal [90%; 242 cases]
```

Figure A.26: CSense analyis showing that thermodynamics controls the furnace operation at the indicated position ruler in the process data

Figure A.27: CSense analyis showing that flow phenomena control the furnace operation at the indicated position ruler in the process data

```
0. IF X_4_Hot_air_2_flow_rate > 8973.00 AND
      X_9_Sinter_HD_ratio      > 2.445
   THEN Y_Zinc_recovery is Normal [100%; 164 cases]
```

Input: X_1_Temperature_of_blast

Resolution: 100

Minimum: 920

Maximum: 1160

Figure A.28: CSense analyis showing that chaotic behaviour in the furnace dominates the operation at the indicated position ruler

In summary *This example makes clear why first principles thermodynamic, kinetic, transfer or fluid flow models on their own can never create good stand-alone models. At most these must be integrated in an intelligent manner to be able to capture all furnace operating states, but this requires enormous computing power and an extreme number of data to parameterise the first principles models. The approach here suggests the use of first principles to derive suitable parameters which characterize all fundamental aspects of the process. These should then be used in empirical non-linear models which can capture all states of the furnace and move easily back and forth between them. This pragmatic approach makes it possible to model the ISF rather accurately!*

Appendix B

Description of metal production flowcharts

In comparison with the well-known examples of eco-industrial parks, the interconnected metal production and recycling systems are a less recognized example of industrial ecology in practice. The metallurgical industries minimized the use of resources and production of wastes by interchanging resources, intermediates and residues between processes. As a result the production of metals is so interdependent that they can hardly be considered separately. The metal production and recycling system is therefore an excellent case to study the potential of the current descriptive approaches to design and manage industrial systems as industrial ecosystems. To date industrial ecology studies on metals production and recycling lack a sufficient depth to invoke improvement for metal processing and recycling systems.

To model the metal production system at sufficient depth, it must be seen as a dynamic network of interdependent process steps that are interconnected through the exchange of intermediates. To enable modelling the system at a sufficient depth, this appendix contains:

- Its application in different end-uses.
- The description and flowsheet of the production of the metal.
- The reconciled mass balances of the processes in the flowsheet.

Note that all this information can also be directly obtained from the model on the supplied CD ROM; for example by clicking on any the Simulink flowchart components, or by browsing through the data "M-files". The product outputs are given as percentage of the total input. The outputs can be divided into three categories:

- *Fluxes*: These are extra inputs usually consisting of SiO_2, CaO and other similar minerals. Although fluxes are inputs they are listed under outputs for mathematical reasons. The need for flux is dependent on the input of metal sources (ore, etc). Note that the sum of recoveries of the other outputs can exceed 100% if fluxes are used in the process.
- *Products and intermediates*: One or several outputs which are processed further or are the end product (metal)
- *Wastes*: Consisting of off gas, flue dust, residues and slag. These are the emissions to the environment which are often further processed before finally to be emitted to the

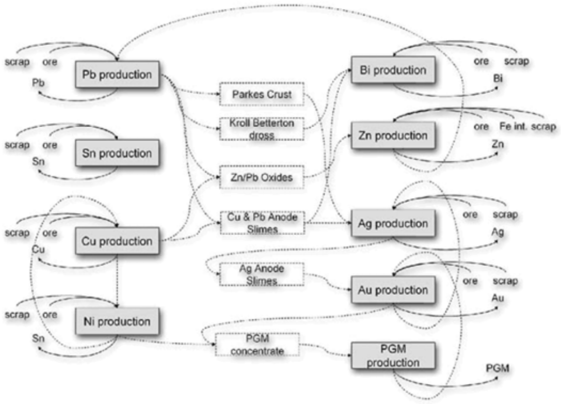


Figure B.1: Overview of the interconnected production system of eleven metals. The dotted squares represent important intermediates connecting the metal production circuits.

environment. If not included in the table recovery to slag follows from: 100% - the recovery of all other streams in %.

- In addition the energy requirements (coal, oil, gas, electricity) and air are listed and, if applicable, the amount of off gas produced in terms of NO_X, CO, CO_2 and SO_2.

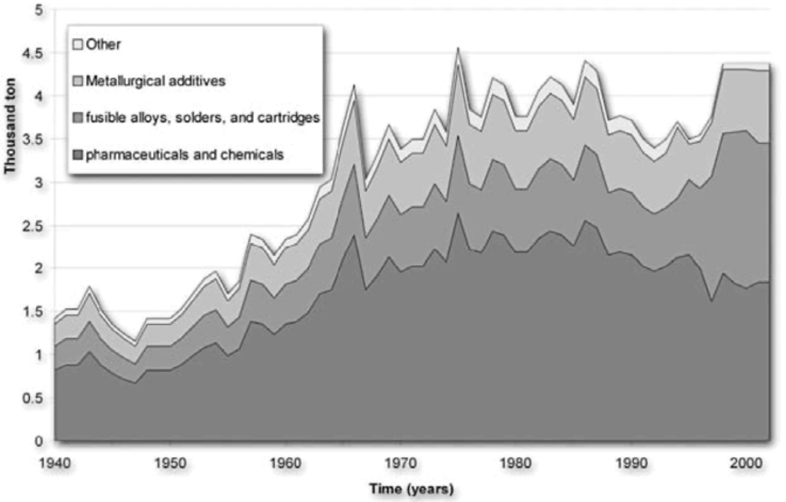


Figure B.2: Bismuth production and estimated end uses from 1940-2000 [227, 463].

B.1 Bismuth production and recycling profile

B.1.1 End uses

In 2000, about 4370 tons of bismuth was produce globally. Based on U.S. consumption patterns, it is estimated that currently about 42% of bismuth is used in bismuth alloys, 40% in pharmaceuticals and chemicals, 16.5% as metallurgical additives, and 1.5% for other uses. In recent years, several new uses for bismuth have been developed as non-toxic substitutes for lead in various applications. These included the use of bismuth in brass plumbing fixtures, ceramic glazes, crystal ware, fishing sinkers, lubricating greases, pigments, and solders. Because data on the end uses of bismuth covered only the last decade, the figure below is constructed using extrapolation.

B.1.2 Production

Bismuth is mostly recovered as by-product from lead and copper production, viz. the copper and lead anode slimes (18%) and the Kroll Betterton dross (61%) from lead production. Only in very rare occasions ores are rich enough in bismuth to treat them separately. The world's only significant potential source where bismuth could be the principal product is the Tasna Mine in Bolivia, which was closed in 1985. Bismuth is also obtained from other bismuth rich concentrates. These concentrates exhibit great variety and there is no standard procedure for treating them, however, a distinction can be made between special refinery (16%) and other (5%) operations.

Bismuth is separated from lead during the Kroll-Betterton process as the *Kroll-Betterton dross*. The dross is mixed with tar oil to oxidize the magnesium and calcium present, while some of the lead is melted and separated (oxidic melting). In subsequent chlorine wash and

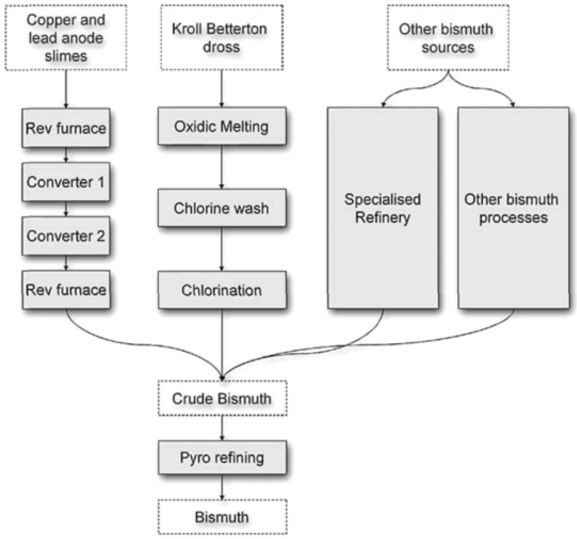


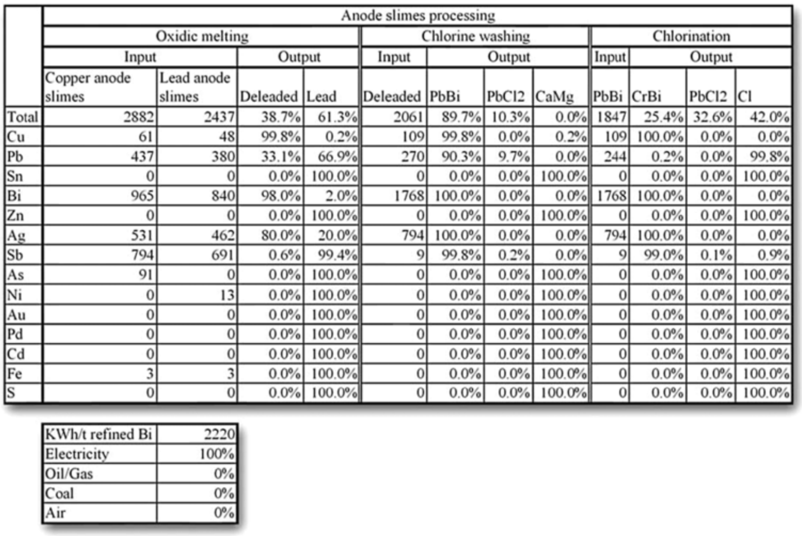
Figure B.3: Simplified bismuth production flowchart chlorination steps, the remaining solid dross is melted and chlorinated. This converts the residual lead to lead-chloride leaving crude bismuth as product. Anode slimes from lead and copper refining can contain significant amounts of bismuth (see Sections B.4 and B.2 respectively). The anode slimes from both processes are treated in a similar way. First, the anode slimes are melted in a reverberatory furnace to partially evaporate the antimony present. Then the metal is air oxidized in a converter in two stages. The resulting product is treated in a second reverberatory furnace to obtain crude bismuth. Refining of bismuth is almost identical to lead refining. Refining is done in five steps:

- de-copperization by liquation and sulphuring,
- tellurium, arsenic and antimony removal with the Harris process,
- removal of precious metals by zinc addition,
- lead and zinc removal by chlorination, and
- the final oxidation with air in the presence of sodium hydroxide (NaOH).

Only a small amount of bismuth is obtained by recycling old scrap. In the recycling of old scrap bismuth is recovered as in the Ferro and non-Ferro fractions. Bismuth in Ferro fractions typically remains in the steel cycle. Part of the bismuth from the non-ferro fractions returns to bismuth production through the copper and lead anode slimes, and the Kroll Betterton dross.

B.1.3 Reconciled mass balances

These data represent the distribution of elements between the indicated phases of the unit operations relevant for processing as depicted by Figure B.3. These have been obtained by closing the mass balances by the use of data reconciliation techniques.



	Anode slimes processing												
	Oxidic melting				Chlorine washing				Chlorination				
	Input		Output		Input	Output			Input	Output			
	Copper anode slimes	Lead anode slimes	Deleaded	Lead	Deleaded	PbBi	PbCl2	CaMg	PbBi	CrBi	PbCl2	Cl	
Total	2882	2437	38.7%	61.3%	2061	89.7%	10.3%	0.0%	1847	25.4%	32.6%	42.0%	
Cu	61	48	99.8%	0.2%	109	99.8%	0.0%	0.2%	109	100.0%	0.0%	0.0%	
Pb	437	380	33.1%	66.9%	270	90.3%	9.7%	0.0%	244	0.2%	0.0%	99.8%	
Sn	0	0	0.0%	100.0%	0	0.0%	0.0%	100.0%	0	0.0%	0.0%	100.0%	
Bi	965	840	98.0%	2.0%	1768	100.0%	0.0%	0.0%	1768	100.0%	0.0%	0.0%	
Zn	0	0	0.0%	100.0%	0	0.0%	0.0%	100.0%	0	0.0%	0.0%	100.0%	
Ag	531	462	80.0%	20.0%	794	100.0%	0.0%	0.0%	794	100.0%	0.0%	0.0%	
Sb	794	691	0.6%	99.4%	9	99.8%	0.2%	0.0%	9	99.0%	0.1%	0.9%	
As	91	0	0.0%	100.0%	0	0.0%	0.0%	100.0%	0	0.0%	0.0%	100.0%	
Ni	0	13	0.0%	100.0%	0	0.0%	0.0%	100.0%	0	0.0%	0.0%	100.0%	
Au	0	0	0.0%	100.0%	0	0.0%	0.0%	100.0%	0	0.0%	0.0%	100.0%	
Pd	0	0	0.0%	100.0%	0	0.0%	0.0%	100.0%	0	0.0%	0.0%	100.0%	
Cd	0	0	0.0%	100.0%	0	0.0%	0.0%	100.0%	0	0.0%	0.0%	100.0%	
Fe	3	3	0.0%	100.0%	0	0.0%	0.0%	100.0%	0	0.0%	0.0%	100.0%	
S	0	0	0.0%	100.0%	0	0.0%	0.0%	100.0%	0	0.0%	0.0%	100.0%	

KWh/t refined Bi	2220
Electricity	100%
Oil/Gas	0%
Coal	0%
Air	0%

Figure B.4: Data refers to recovery % from anode slimes in Figure B.3

	Kroll Bretterton crust processing														
	Reverberatory furnace 1			Converter 1				Converter 2				Reverberatory furnace 2			
	Input	Output		Input	Output			Input	Output			Input	Output		
	Kroll Bretterton crust	Slag	Flue dust	Slag	Metal	Flue dust	Slag	Metal	Bismuth slag	AgBiPb	Flue dust	Bismuth slag	Crude bismuth	Copper matte	slag
Total	5319	88.5%	11.5%	4706	68.5%	2.9%	28.6%	3222	61.5%	32.5%	6.0%	1983	42.1%	14.5%	43.3%
Cu	110	96.6%	3.4%	106	82.9%	4.2%	12.9%	88	100.0%	0.0%	0.0%	88	31.6%	68.4%	0.0%
Pb	817	79.2%	20.8%	648	57.9%	4.0%	38.2%	375	68.3%	23.5%	8.1%	256	24.3%	9.8%	66.0%
Sn	0	0.0%	100.0%	0	0.0%	0.0%	100.0%	0	0.0%	0.0%	100.0%	0	0.0%	0.0%	100.0%
Bi	1805	96.2%	3.8%	1736	85.5%	1.8%	12.6%	1485	62.7%	30.1%	7.2%	931	89.5%	1.1%	9.4%
Zn	0	0.0%	100.0%	0	0.0%	0.0%	100.0%	0	0.0%	0.0%	100.0%	0	0.0%	0.0%	100.0%
Ag	992	93.7%	6.3%	930	81.4%	1.7%	16.9%	757	5.5%	91.6%	2.8%	42	84.3%	8.9%	6.8%
Sb	1485	76.4%	23.6%	1134	12.6%	4.3%	83.1%	143	40.7%	0.0%	59.3%	58	0.3%	29.4%	70.3%
As	91	0.0%	100.0%	0	0.0%	0.0%	100.0%	0	0.0%	0.0%	100.0%	0	0.0%	0.0%	100.0%
Ni	13	0.0%	100.0%	0	0.0%	0.0%	100.0%	0	0.0%	0.0%	100.0%	0	0.0%	0.0%	100.0%
Au	0	5.8%	94.2%	0	0.0%	0.0%	100.0%	0	0.0%	0.0%	100.0%	0	0.0%	0.0%	100.0%
Pd	0	0.0%	100.0%	0	0.0%	0.0%	100.0%	0	0.0%	0.0%	100.0%	0	0.0%	0.0%	100.0%
Cd	0	0.0%	100.0%	0	0.0%	0.0%	100.0%	0	0.0%	0.0%	100.0%	0	0.0%	0.0%	100.0%
Fe	7	0.0%	100.0%	0	0.0%	0.0%	100.0%	0	0.0%	0.0%	100.0%	0	0.0%	0.0%	100.0%
S	0	0.0%	100.0%	0	0.0%	0.0%	100.0%	0	0.0%	0.0%	100.0%	0	0.0%	0.0%	100.0%

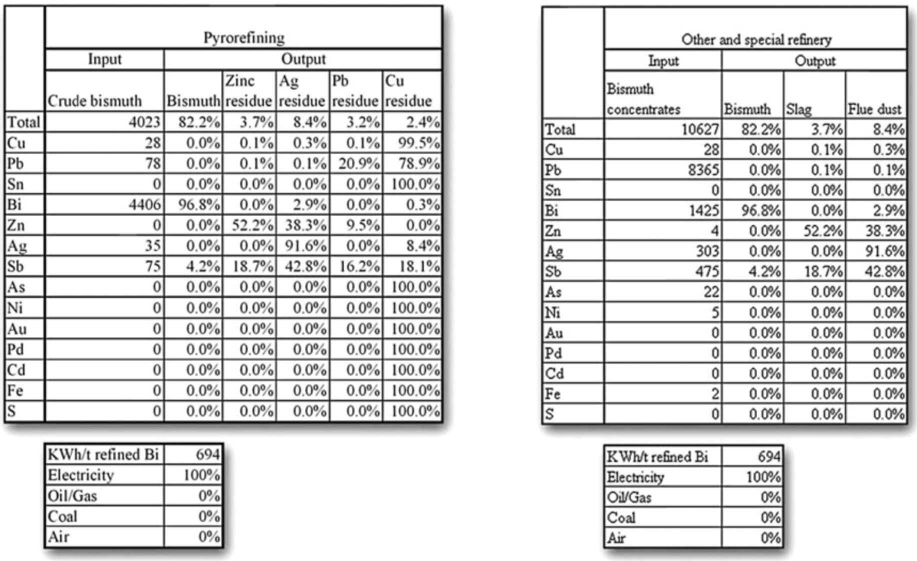
KWh/t refined Bi	4530
Electricity	0%
Oil/Gas	70%
Coal	0%
Air	30%

KWh/t refined Bi	386
Electricity	72%
Oil/Gas	0%
Coal	28%
Air	0%

KWh/t refined Bi	386
Electricity	72%
Oil/Gas	0%
Coal	28%
Air	0%

KWh/t refined Bi	4530
Electricity	0%
Oil/Gas	70%
Coal	0%
Air	30%

Figure B.5: Data refers to recovery % from Kroll-Betterton crust in Figure B.3



	Pyrorefining					
	Input	Output				
	Crude bismuth	Bismuth	Zinc residue	Ag residue	Pb residue	Cu residue
Total	4023	82.2%	3.7%	8.4%	3.2%	2.4%
Cu	28	0.0%	0.1%	0.3%	0.1%	99.5%
Pb	78	0.0%	0.1%	0.1%	20.9%	78.9%
Sn	0	0.0%	0.0%	0.0%	0.0%	100.0%
Bi	4406	96.8%	0.0%	2.9%	0.0%	0.3%
Zn	0	0.0%	52.2%	38.3%	9.5%	0.0%
Ag	35	0.0%	0.0%	91.6%	0.0%	8.4%
Sb	75	4.2%	18.7%	42.8%	16.2%	18.1%
As	0	0.0%	0.0%	0.0%	0.0%	100.0%
Ni	0	0.0%	0.0%	0.0%	0.0%	100.0%
Au	0	0.0%	0.0%	0.0%	0.0%	100.0%
Pd	0	0.0%	0.0%	0.0%	0.0%	100.0%
Cd	0	0.0%	0.0%	0.0%	0.0%	100.0%
Fe	0	0.0%	0.0%	0.0%	0.0%	100.0%
S	0	0.0%	0.0%	0.0%	0.0%	100.0%

KWh/t refined Bi	694
Electricity	100%
Oil/Gas	0%
Coal	0%
Air	0%

	Other and special refinery			
	Input	Output		
	Bismuth concentrates	Bismuth	Slag	Flue dust
Total	10627	82.2%	3.7%	8.4%
Cu	28	0.0%	0.1%	0.3%
Pb	8365	0.0%	0.1%	0.1%
Sn	0	0.0%	0.0%	0.0%
Bi	1425	96.8%	0.0%	2.9%
Zn	4	0.0%	52.2%	38.3%
Ag	303	0.0%	0.0%	91.6%
Sb	475	4.2%	18.7%	42.8%
As	22	0.0%	0.0%	0.0%
Ni	5	0.0%	0.0%	0.0%
Au	0	0.0%	0.0%	0.0%
Pd	0	0.0%	0.0%	0.0%
Cd	0	0.0%	0.0%	0.0%
Fe	2	0.0%	0.0%	0.0%
S	0	0.0%	0.0%	0.0%

KWh/t refined Bi	694
Electricity	100%
Oil/Gas	0%
Coal	0%
Air	0%

Figure B.6: Data refers to recovery % during various refining steps in Figure B.3

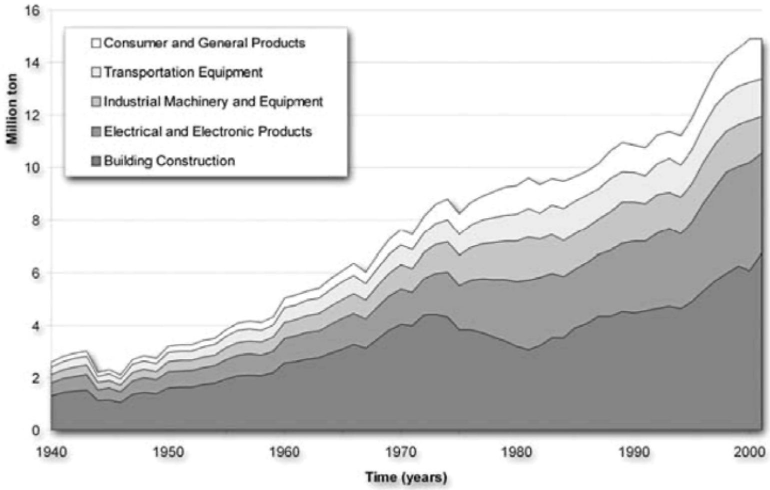


Figure B.7: Copper production and estimated end uses from 1940-2000 [227, 226, 464, 465].

B.2 Copper production and recycling profile

B.2.1 End uses

In 2000, about 14.9 million t tons of copper were produced globally [227]. Copper is an essential metal for electronic appliances, because of its excellent electrical conductivity. Electrical uses of copper, including power transmission and generation, building wiring, telecommunication, and electrical and electronic products, account for about three quarters of total copper use. Building construction is the single largest market, followed by electronics and electronic products, transportation, industrial machinery, and consumer and general products.

B.2.2 Production

Copper is produced from sulphuric and oxidic ores that are obtained from lead, zinc, nickel and copper mining. A copper ore has often a low copper content, 0.8-4%, and is crushed, ground and concentrated by flotation to 25-35% Cu [466, 256, 404][1]. The resulting tailings have a very low copper content (ca. 0.05% Cu), and are discarded. Dependent on ore composition, copper is produced from the ore concentrates through different routes.

About 80% [466] of the primary copper originates from low-grade sulphide ores (containing ca. 0.5-2% Cu [404]). These are usually converted into copper in two main steps:

- The concentrate is smelted to a matte, and then converted to crude (blister or converter) copper, and
- the crude copper is pyrometallurgical refined to fire-refined copper and subsequently electrolytically to high purity copper.

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[1] Biswas and Davenport [404] report a figure of 20-30%

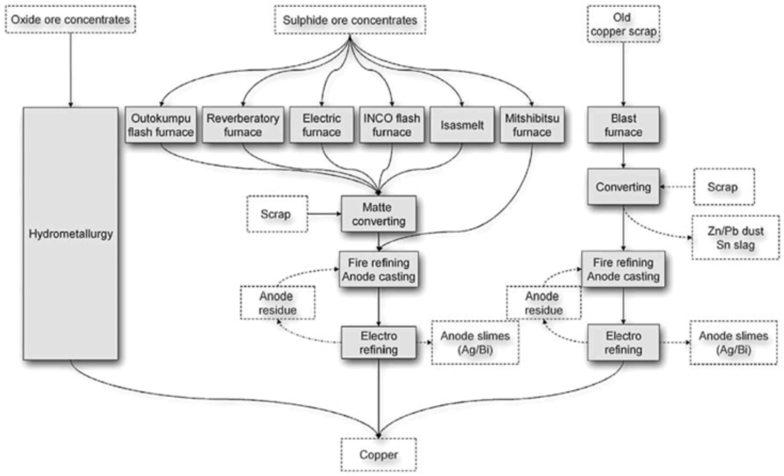

Figure B.8: Simplified copper production flowchart

Prior to smelting the copper concentrate to "matte" in the pyrometallurgical route, roasting may be necessary to decrease the sulphur content to an optimum level for smelting. In many modern processes, the roasting step is combined with matte smelting. In matte smelting the concentrate, or roasting product, is converted into a copper matte that consists of approximately 55% copper, 20% sulphur, 15% iron and some minor elements. Globally, six different processes are used for matte smelting, viz. reverberatory furnace smelting (27%), electric furnace smelting (8%), Outokumpu flash smelting (48%), Inco flash smelting (8%), Isa or Ausmelt (5%), and the Mitsubishi process (5%) [467]. The reverberatory furnace is a classic, rectangular furnace with burners at one side of the furnace. In the furnace, two zones can be distinguished: the smelting and settling zones. The concentrate, flux and fuel (coal, heavy fuel oil or natural gas) are fed into the furnace at the smelting zone located at the burner side. After smelting, the reactor mixture flows to the opposite side of the furnaces, the settling zone, where matte and slag separate. The atmosphere in the furnace is slightly oxidizing, or neutral. The reverberatory furnace has the highest energy consumption of all copper matte-smelting operations. The reverberatory furnace is an old technique for copper smelting; new furnaces of this type will probably not be built. The electric furnace process is similar to the reverberatory furnace, but the feed is dried before charging and the furnace is heated by up to six carbon electrodes with alternating currents. As it uses significant amounts of electricity this furnace is usually used only when electricity is inexpensive. The use of electrodes allows higher temperatures, which has the advantage that magnetite can be easier slagged off compared to the reverberatory furnace. In addition, the volume of off gas is smaller and the heat loss is much smaller than in the reverberatory furnaces. The off gas is more easily cleaned.

The Inco Flash furnace, the Outokumpu flash furnace and the Isasmelt are modern autogenous smelters that use the heat generated by the oxidation of iron sulphides for the smelting process. Not only does this save energy input, it also reduces the offgas volumes, moreover the rate of reaction in autogenous smelters is higher which increases production rate. A typical disadvantage is higher copper content in the slag. The Outokumpu flash furnace consists of three distinct sections:

- A circular reaction shaft for roasting and smelting of the dried concentrate,
- a settling hearth for the collection of the molten droplets, and separation of the matte from the slag and
- a rectangular uptake shaft for off gas. In the Outokumpu flash furnace air or oxygen enriched air is used.

The Inco Flash smelting process is very similar to the Outokumpu flash smelting, but is less common. The main difference between the two processes is the use of pure oxygen in the Inco Flash smelting process. The Isasmelt furnace is a tall cylindrical furnace. The feed is heated, and converted by blowing oxygen-enriched air through a lance submerged into the slag. Additional energy can be fed to the process by adding coal to the charge or blowing oil or gas through the lance. The smelted matte from these processes must be further processed in a Peirce-Smith convertor , to produce a crude copper with 98-99% copper suitable for refining (e.g. Ullmann [466], Biswas and Davenport [404]). In this process, the matte is blown with air in two stages. First, the iron is oxidized to iron oxide and dissolved the slag by adding silica. Second, the copper sulphide is converted to copper metal. Because these reactions are highly exothermic, copper scrap is added during the process as a coolant. The last matte smelting process is the Mitsubishi process. The three-step continuous Mitsubishi process combines matte smelting and matte converting. Unlike the other smelting processes, the Mitsubishi process produces crude copper suitable for refining. In the first step, the concentrate is smelted together with fluxes and coal to produce matte, in the second step the matte is separated from the slag in an electric furnace by adding coke and some pyrite, and finally in the last stage the matte is converted into crude copper by oxidation in a continuous converter operating with a ferrite slag from the obtained high-grade matte. The crude copper metal is further refined through fire refining and electrolysis. The fire refining process has three purposes:

- To remove impurities by dissolving in the slag and volatilization,
- to reduce the sulphur content by oxidation, and
- decrease the oxygen content by reduction.

After fire refining the main impurities consists of precious metals, and the copper can be cast into anodes. Fire refining is a batch process using either a reverberatory furnace, or a rotary furnace. The copper concentrate obtained from fire refining is typically further refined by electrolysis. By running a current from the anode to the cathode, a "clean" copper sheet, the copper dissolves and is deposited at the cathode. Base metals, mainly nickel, dissolve into the electrolyte and will be treated to remove the metals. Precious metals do not dissolve and report to the anode slimes; these are treated to remove the precious metals. Approximately 15% of the primary copper originates from low-grade oxidized or mixed ores [466]. Copper is generally produced from these ores through the hydrometallurgical route. The route consists of four steps. In the first step, the ore concentrate is pre-treated, either physically or chemically. In the second step, the concentrate is leached with sulphuric acid or ammoniacal solutions. Subsequently, this solution is cleaned by precipitation of impurities or by selective enrichment of copper by solvent extraction or ion exchange. In the fourth step, the cleaned solution is precipitated to copper metal. The remaining primary copper comes from high-grade ores and is processed in shaft furnaces. Copper from secondary material, which often has a high copper content and low sulphur content, is usually recovered through this route. A blast or shaft furnace is fed with alternating layers of copper containing materials and coke. The blast furnace can be divided into three zones:

- The heating zone where the water is evaporated,
- the reduction zone where reactions between gases and solids take place,
- the smelting zone where the liquid phases react with each other.

The furnace produces black copper with approximately 75% copper, copper rich slag and if there are high concentrations of arsenic or antimony a third phase, speiss, can form. The black copper is converted to crude copper in a similar way to primary converting. Lead, tin and nickel report to the slag phase, zinc and some lead report to the flue dust. Some 12.7% of copper is obtained by recycling old scrap [227]. The bulk of the old copper scrap is recovered for its copper value. The Ferro fractions and old lead scrap resulting from the waste separation processes also contain small amounts of copper. Copper in Ferro fractions is typically removed from the steel cycle in the iron production slag. The copper from the old lead scrap fractions can be recovered. Low-grade old copper scrap is typically recovered in a blast furnace, an Ausmelt reactor, and high grade copper scrap can directly be processed in a converter, or even directly refined[2]. In addition, also old and new scrap is added to control the temperature in the ("primary") convertors. Tin is a valuable by-product of secondary copper production. The tin can be recovered in a silicate slag (at the copper convertors) which is sold to tin producers (up to 17-25% Sn, [468]). Zinc and lead are recovered as the oxides in the blast furnace and convertors. The refining of the convertor scrap is similar to the "primary" refining.

B.2.3 Reconciled mass balances

These data represent the distribution of elements between the indicated phases of the unit operations relevant for processing as depicted by Figure B.8. These have been obtained by closing the mass balances by the use of data reconciliation techniques.

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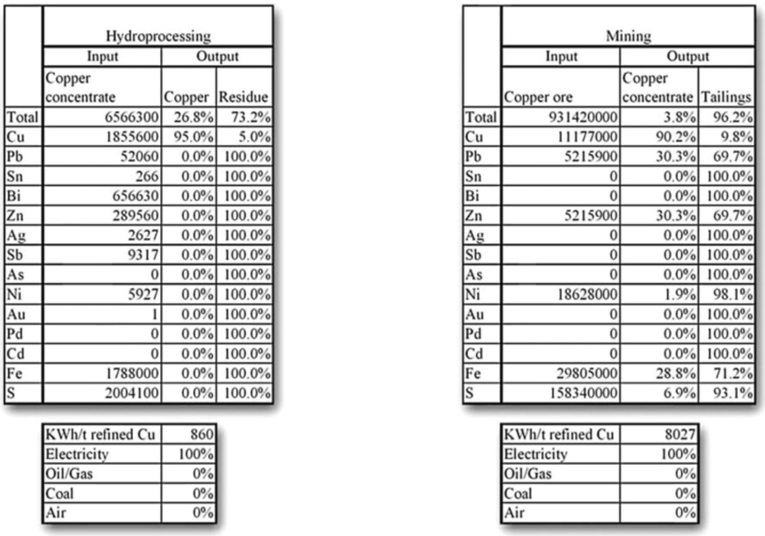
[2] Some copper scrap (e.g wire, cable and copper tubing) can be separated in relatively pure copper, and needs only to be remelted and cast. For instance, copper wire is chopped into short pieces for easy disposal of insulation, and finally melted in a convertor (typically a reverberatory furnace) and cast. Brass and bronze scrap are generally remelted without refining as well, provided they can be sorted into composition categories [241]



	Hydroprocessing		
	Input	Output	
	Copper concentrate	Copper	Residue
Total	6566300	26.8%	73.2%
Cu	1855600	95.0%	5.0%
Pb	52060	0.0%	100.0%
Sn	266	0.0%	100.0%
Bi	656630	0.0%	100.0%
Zn	289560	0.0%	100.0%
Ag	2627	0.0%	100.0%
Sb	9317	0.0%	100.0%
As	0	0.0%	100.0%
Ni	5927	0.0%	100.0%
Au	1	0.0%	100.0%
Pd	0	0.0%	100.0%
Cd	0	0.0%	100.0%
Fe	1788000	0.0%	100.0%
S	2004100	0.0%	100.0%

KWh/t refined Cu	860
Electricity	100%
Oil/Gas	0%
Coal	0%
Air	0%

	Mining		
	Input	Output	
	Copper ore	Copper concentrate	Tailings
Total	931420000	3.8%	96.2%
Cu	11177000	90.2%	9.8%
Pb	5215900	30.3%	69.7%
Sn	0	0.0%	100.0%
Bi	0	0.0%	100.0%
Zn	5215900	30.3%	69.7%
Ag	0	0.0%	100.0%
Sb	0	0.0%	100.0%
As	0	0.0%	100.0%
Ni	18628000	1.9%	98.1%
Au	0	0.0%	100.0%
Pd	0	0.0%	100.0%
Cd	0	0.0%	100.0%
Fe	29805000	28.8%	71.2%
S	158340000	6.9%	93.1%

KWh/t refined Cu	8027
Electricity	100%
Oil/Gas	0%
Coal	0%
Air	0%

Figure B.9: Data refers to recovery % in Mining and hydro-processing in Figure B.8

	Primary smelting 1																	
	Electric furnace						Outokumpu flash furnace					Inco flash furnace						
	Input	Output					Input	Output				Input	Output					
	Copper concentrate	Flux	Matte	Flue dust	Offgas	Slag	Copper concentrate	Matte	Flue dust	Offgas	Slag	Copper concentrate	Flux	Matte	Flue dust	Offgas	Slag
Total	2393000	3.7%	46.1%	14.9%	10.9%	31.7%	14657000	42.8%	6.1%	12.4%	38.8%	2093900	14.1%	46.4%	2.3%	9.5%	56.0%
Cu	673640	0.0%	89.4%	10.6%	0.0%	0.0%	4126100	82.8%	5.3%	0.0%	11.8%	589440	0.0%	89.9%	1.8%	0.0%	8.3%
Pb	14358	0.0%	39.8%	0.1%	0.0%	60.1%	102600	31.5%	62.0%	0.0%	6.5%	9004	0.0%	55.6%	42.1%	0.0%	2.3%
Sn	718	0.0%	1.6%	0.0%	0.0%	98.5%	0	42.8%	6.1%	0.0%	51.2%	0	0.0%	18.5%	0.0%	3.8%	77.7%
Bi	239	0.0%	16.1%	0.0%	0.0%	83.9%	1466	42.8%	6.1%	0.0%	51.2%	209	0.0%	34.4%	0.0%	8.4%	57.2%
Zn	105530	0.0%	13.6%	0.0%	0.0%	86.4%	646390	12.6%	10.7%	0.0%	76.7%	92342	0.0%	13.6%	11.4%	0.0%	75.0%
Ag	957	0.0%	100.0%	0.0%	0.0%	0.0%	5863	95.0%	5.0%	0.0%	0.0%	838	0.0%	100.0%	0.0%	0.0%	0.0%
Sb	239	0.0%	6.7%	0.0%	0.0%	93.3%	14657	42.8%	6.1%	0.0%	51.2%	2094	0.0%	50.0%	0.0%	8.5%	41.5%
As	0	0.0%	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%
Ni	239	0.0%	7.7%	0.0%	0.0%	92.3%	1466	7.1%	0.0%	0.0%	92.9%	209	0.0%	7.7%	0.0%	0.0%	92.3%
Au	0	0.0%	100.0%	0.0%	0.0%	0.0%	0	98.0%	2.0%	0.0%	0.0%	0	0.0%	100.0%	0.0%	0.0%	0.0%
Pd	0	0.0%	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%
Cd	0	0.0%	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%
Fe	606400	0.0%	30.3%	8.8%	0.0%	60.9%	4104100	25.4%	2.4%	0.0%	72.2%	607230	0.0%	26.6%	1.0%	0.0%	72.3%
S	734430	0.0%	32.7%	4.7%	32.0%	30.6%	4470500	30.5%	2.5%	40.7%	26.4%	638640	0.0%	33.1%	1.1%	27.5%	38.3%

KWh/t refined Cu	3290
Electricity	72%
Oil/Gas	0%
Coal	28%
Air	0%
CO	0.00.E+00
CO2	0.00.E+00
SO2	1.60.E+08
NOX	5.72.E+08

KWh/t refined Cu	1854
Electricity	0%
Oil/Gas	65%
Coal	0%
Air	35%
CO	0.00.E+00
CO2	0.00.E+00
SO2	6.20.E+08
NOX	2.89.E+09

KWh/t refined Cu	640
Electricity	0%
Oil/Gas	74%
Coal	0%
Air	35%
CO	0.00.E+00
CO2	0.00.E+00
SO2	1.20.E+08
NOX	4.94.E+08

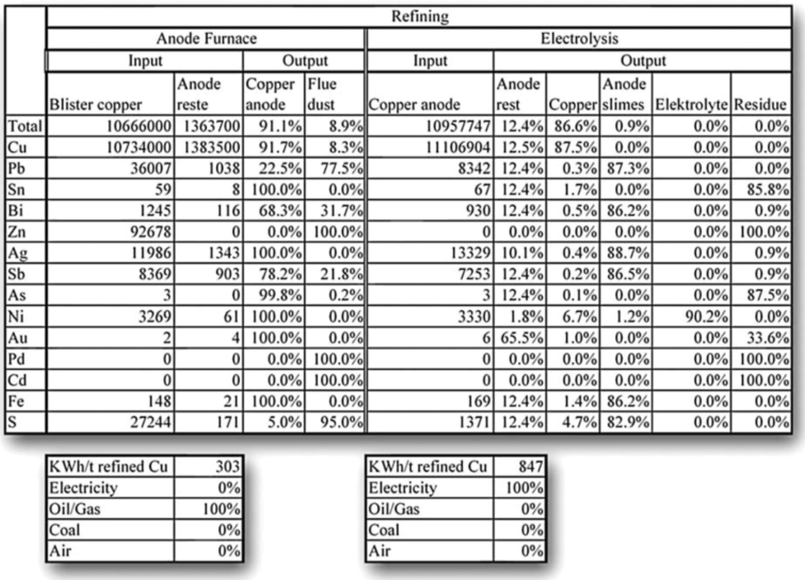
Figure B.10: Data refers to recovery % in primary smelting in Figure B.8

	Primary converting														
	Mitsibishu process							Matte smelting							
	Input	Output						Input		Output					
	Copper concentrate	Flux	Blister copper	Flue dust	Offgas	Converter slag	Smelting slag	Matte	Copper scrap	Flux	Blister copper	Flue dust	Offgas	Slag
Total	1794800	11.9%	28.2%	4.2%	29.4%	10.1%	39.9%	12482000	3769900	12.7%	62.5%	0.4%	24.4%	25.3%
Cu	538080	0.0%	92.6%	1.8%	0.0%	4.8%	0.8%	6807400	3769600	0.0%	96.8%	0.1%	0.0%	3.1%
Pb	22614	0.0%	9.0%	80.2%	0.0%	0.0%	10.9%	64278	4	0.0%	52.9%	20.8%	0.0%	26.3%
Sn	179	0.0%	28.2%	29.7%	0.0%	10.1%	32.0%	11	2	0.0%	62.5%	24.4%	0.0%	13.0%
Bi	179	0.0%	49.1%	29.8%	0.0%	10.1%	11.0%	1166	3	0.0%	99.0%	1.0%	0.0%	0.0%
Zn	79096	0.0%	9.0%	80.2%	0.0%	0.0%	10.9%	161920	1	0.0%	52.9%	20.8%	0.0%	26.3%
Ag	718	0.0%	100.0%	0.0%	0.0%	0.0%	0.0%	11243	26	0.0%	100.0%	0.0%	0.0%	0.0%
Sb	179	0.0%	61.0%	13.4%	0.0%	7.7%	18.0%	8420	4	0.0%	99.0%	1.0%	0.0%	0.0%
As	0	0.0%	0.0%	0.0%	0.0%	0.0%	100.0%	0	3	0.0%	99.0%	1.0%	0.0%	0.0%
Ni	17948	0.0%	16.9%	0.0%	0.0%	0.0%	83.1%	208	4	0.0%	100.0%	0.0%	0.0%	0.0%
Au	2	0.0%	100.0%	0.0%	0.0%	0.0%	0.0%	0	0	0.0%	59.0%	0.0%	0.0%	41.0%
Pd	0	0.0%	0.0%	0.0%	0.0%	0.0%	100.0%	0	0	0.0%	0.0%	0.0%	0.0%	100.0%
Cd	0	0.0%	0.0%	0.0%	0.0%	0.0%	100.0%	0	0	0.0%	0.0%	0.0%	0.0%	100.0%
Fe	430390	0.0%	0.0%	2.2%	0.0%	19.4%	78.4%	2078600	5	0.0%	0.0%	0.4%	0.0%	99.6%
S	547410	0.0%	0.2%	1.6%	90.4%	0.4%	7.4%	2718000	24	0.0%	1.0%	0.3%	90.8%	8.0%

KWh/t refined Cu	2566
Electricity	11%
Oil/Gas	6%
Coal	83%
Air	0%
CO	0.00.E+00
CO2	0.00.E+00
SO2	3.37.E+08
NOX	8.76.E+08

KWh/t refined Cu	385
Electricity	0%
Oil/Gas	70%
Coal	0%
Air	30%
CO	0.00.E+00
CO2	0.00.E+00
SO2	1.68.E+09
NOX	5.02.E+09

Figure B.11: Data refers to recovery % in primary converting in Figure B.8

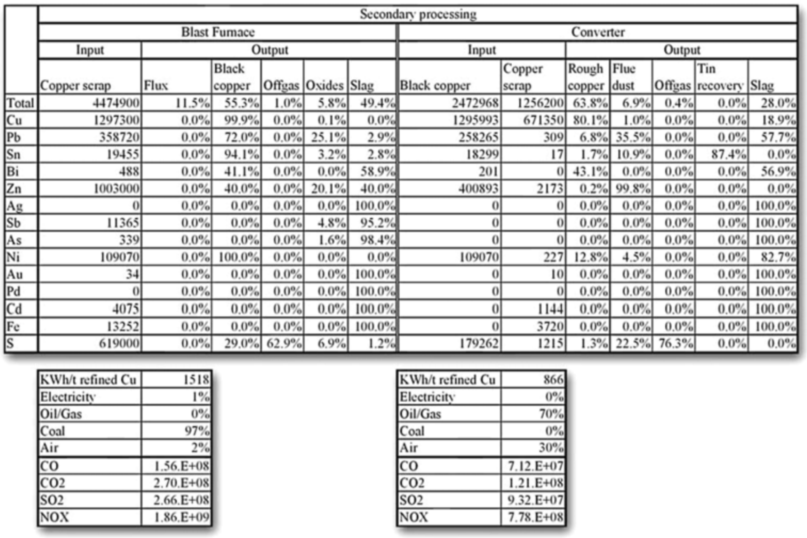


	Refining									
	Anode Furnace				Electrolysis					
	Input		Output		Input	Output				
	Blister copper	Anode reste	Copper anode	Flue dust	Copper anode	Anode rest	Copper	Anode slimes	Elektrolyte	Residue
Total	10666000	1363700	91.1%	8.9%	10957747	12.4%	86.6%	0.9%	0.0%	0.0%
Cu	10734000	1383500	91.7%	8.3%	11106904	12.5%	87.5%	0.0%	0.0%	0.0%
Pb	36007	1038	22.5%	77.5%	8342	12.4%	0.3%	87.3%	0.0%	0.0%
Sn	59	8	100.0%	0.0%	67	12.4%	1.7%	0.0%	0.0%	85.8%
Bi	1245	116	68.3%	31.7%	930	12.4%	0.5%	86.2%	0.0%	0.9%
Zn	92678	0	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%
Ag	11986	1343	100.0%	0.0%	13329	10.1%	0.4%	88.7%	0.0%	0.9%
Sb	8369	903	78.2%	21.8%	7253	12.4%	0.2%	86.5%	0.0%	0.9%
As	3	0	99.8%	0.2%	3	12.4%	0.1%	0.0%	0.0%	87.5%
Ni	3269	61	100.0%	0.0%	3330	1.8%	6.7%	1.2%	90.2%	0.0%
Au	2	4	100.0%	0.0%	6	65.5%	1.0%	0.0%	0.0%	33.6%
Pd	0	0	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%
Cd	0	0	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%
Fe	148	21	100.0%	0.0%	169	12.4%	1.4%	86.2%	0.0%	0.0%
S	27244	171	5.0%	95.0%	1371	12.4%	4.7%	82.9%	0.0%	0.0%

KWh/t refined Cu	303
Electricity	0%
Oil/Gas	100%
Coal	0%
Air	0%

KWh/t refined Cu	847
Electricity	100%
Oil/Gas	0%
Coal	0%
Air	0%

Figure B.12: Data refers to recovery % in refining in Figure B.8

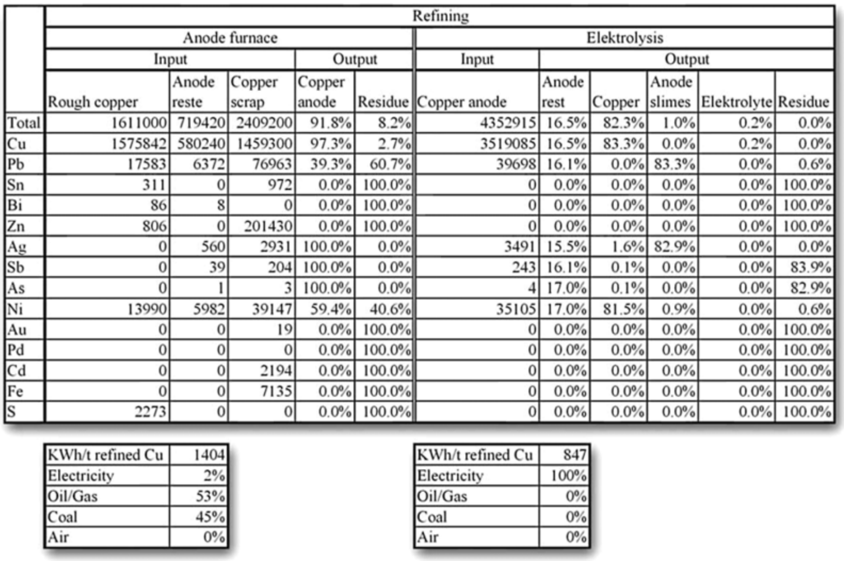


	Secondary processing												
	Blast Furnace						Converter						
	Input	Output					Input		Output				
	Copper scrap	Flux	Black copper	Offgas	Oxides	Slag	Black copper	Copper scrap	Rough copper	Flue dust	Offgas	Tin recovery	Slag
Total	4474900	11.5%	55.3%	1.0%	5.8%	49.4%	2472968	1256200	63.8%	6.9%	0.4%	0.0%	28.0%
Cu	1297300	0.0%	99.9%	0.0%	0.1%	0.0%	1295993	671350	80.1%	1.0%	0.0%	0.0%	18.9%
Pb	358720	0.0%	72.0%	0.0%	25.1%	2.9%	258265	309	6.8%	35.5%	0.0%	0.0%	57.7%
Sn	19455	0.0%	94.1%	0.0%	3.2%	2.8%	18299	17	1.7%	10.9%	0.0%	87.4%	0.0%
Bi	488	0.0%	41.1%	0.0%	0.0%	58.9%	201	0	43.1%	0.0%	0.0%	0.0%	56.9%
Zn	1003000	0.0%	40.0%	0.0%	20.1%	40.0%	400893	2173	0.2%	99.8%	0.0%	0.0%	0.0%
Ag	0	0.0%	0.0%	0.0%	0.0%	100.0%	0	0	0.0%	0.0%	0.0%	0.0%	100.0%
Sb	11365	0.0%	0.0%	0.0%	4.8%	95.2%	0	0	0.0%	0.0%	0.0%	0.0%	100.0%
As	339	0.0%	0.0%	0.0%	1.6%	98.4%	0	0	0.0%	0.0%	0.0%	0.0%	100.0%
Ni	109070	0.0%	100.0%	0.0%	0.0%	0.0%	109070	227	12.8%	4.5%	0.0%	0.0%	82.7%
Au	34	0.0%	0.0%	0.0%	0.0%	100.0%	0	10	0.0%	0.0%	0.0%	0.0%	100.0%
Pd	0	0.0%	0.0%	0.0%	0.0%	100.0%	0	0	0.0%	0.0%	0.0%	0.0%	100.0%
Cd	4075	0.0%	0.0%	0.0%	0.0%	100.0%	0	1144	0.0%	0.0%	0.0%	0.0%	100.0%
Fe	13252	0.0%	0.0%	0.0%	0.0%	100.0%	0	3720	0.0%	0.0%	0.0%	0.0%	100.0%
S	619000	0.0%	29.0%	62.9%	6.9%	1.2%	179262	1215	1.3%	22.5%	76.3%	0.0%	0.0%

KWh/t refined Cu	1518
Electricity	1%
Oil/Gas	0%
Coal	97%
Air	2%
CO	1.56.E+08
CO2	2.70.E+08
SO2	2.66.E+08
NOX	1.86.E+09

KWh/t refined Cu	866
Electricity	0%
Oil/Gas	70%
Coal	0%
Air	30%
CO	7.12.E+07
CO2	1.21.E+08
SO2	9.32.E+07
NOX	7.78.E+08

Figure B.13: Data refers to recovery % in secondary smelting in Figure B.8



	Refining										
	Anode furnace					Elektrolysis					
	Input			Output		Input	Output				
	Rough copper	Anode reste	Copper scrap	Copper anode	Residue	Copper anode	Anode rest	Copper	Anode slimes	Elektrolyte	Residue
Total	1611000	719420	2409200	91.8%	8.2%	4352915	16.5%	82.3%	1.0%	0.2%	0.0%
Cu	1575842	580240	1459300	97.3%	2.7%	3519085	16.5%	83.3%	0.0%	0.2%	0.0%
Pb	17583	6372	76963	39.3%	60.7%	39698	16.1%	0.0%	83.3%	0.0%	0.6%
Sn	311	0	972	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%
Bi	86	8	0	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%
Zn	806	0	201430	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%
Ag	0	560	2931	100.0%	0.0%	3491	15.5%	1.6%	82.9%	0.0%	0.0%
Sb	0	39	204	100.0%	0.0%	243	16.1%	0.1%	0.0%	0.0%	83.9%
As	0	1	3	100.0%	0.0%	4	17.0%	0.1%	0.0%	0.0%	82.9%
Ni	13990	5982	39147	59.4%	40.6%	35105	17.0%	81.5%	0.9%	0.0%	0.6%
Au	0	0	19	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%
Pd	0	0	0	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%
Cd	0	0	2194	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%
Fe	0	0	7135	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%
S	2273	0	0	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%

KWh/t refined Cu	1404
Electricity	2%
Oil/Gas	53%
Coal	45%
Air	0%

KWh/t refined Cu	847
Electricity	100%
Oil/Gas	0%
Coal	0%
Air	0%

Figure B.14: Data refers to recovery % in refining in Figure B.8

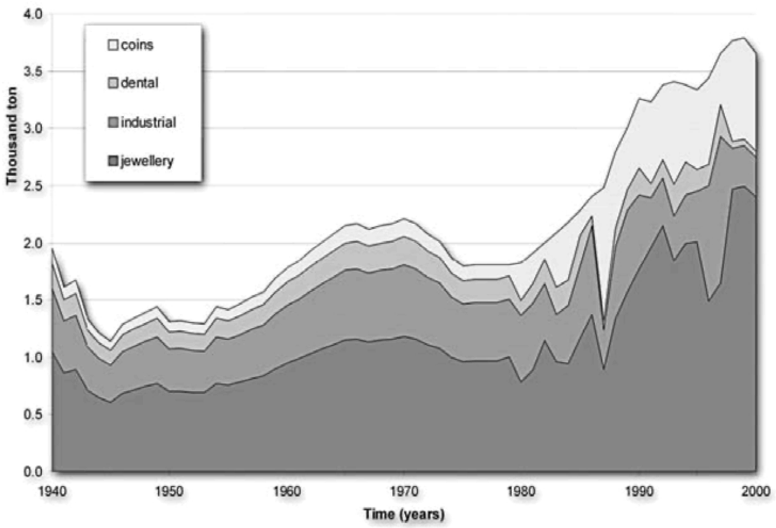


Figure B.15: Gold production and estimated end uses from 1940-2000 [227]

B.3 Gold production and recycling profile

B.3.1 End uses

In 2000, about 3660 tons of gold were produced globally [227]. Gold is a valuable, yellow-coloured scarce metal that has been the inspiration for innumerable conquests, wars, and provided impetus for the discovery and exploration of the Western Hemisphere. The voyages of Columbus, Magellan, and other explorers were motivated at least in part by the expectation of finding gold. Spanish conquistadors plundered the sixteenth century Latin American empires, and later other European settlers began to tap the resources in the northern part of the continent. Since the gold decorated the Egyptian life and afterlife, coins, jewellry, and ornaments have always been the most important applications of gold. Still today, they consume most of the gold. In addition to aesthetic characteristics, gold is increasingly valued for its other characteristics, such as malleability, high electrical conductivity, and resistance to oxidation and most chemical agents. Other important end uses for gold are industrial and dental applications. In the 90s about a quarter of the gold was used for industrial applications on average, and less than 10% for dental applications. Because of the use of gold for durable goods such as jewellry and coins, gold can be expected to have an average long residence time in the consumption phase.

B.3.2 Production

The bulk of the gold is obtained from gold ores (76%). A small amount of gold is produced through silver production; this gold originates from copper, lead, silver and nickel ores. Gold concentration processes usually consist of gravity concentration, flotation, cyanidation, or a combination of these processes. Gold ores are mainly treated with the carbon-in-pulp process

[469]. In this process, the gold in ore is dissolved by leaching with cyanide, and subsequently selectively absorbed by active carbon. In the next step, the gold is separated from the carbon, by a second cyanide leach but at a lower pH. Gold is recovered from the leach solution by either electrowinning or precipitation with zinc. The resulting gold concentrate is treated with roasting, smelting or retorting to remove residual impurities, and a suitable feedstock, gold bullion, for the refining process is obtained.

The gold bullion is refined in the Miller process to a grade of 99.5%. The process is based on the low reactivity of gold with chloride at 1100°C: Gold chlorides do not form, while silver and base metals react with chlorine to form stable chlorides. As a consequence, copper and silver are liquid at 1100°C and can be collected in the added borax slag; other base metals vapourize and report to the off gas. The borax slag is treated to recover the silver. In the Wohlwill electrolysis process gold is further refined to a quality of 99.99%. Palladium and platinum are recovered from the electrolyte, a hydrochloric acid/tetrachloroauric acid. Other platinum group metals and silver accumulate in the anode slime. These are further treated to obtain the precious metals. A significant amount of gold is produced from old gold scrap (24%, [227]). Gold's main applications, such as jewellry, require it to be in an almost pure state. Recycling of gold, therefore, usually only involves remelting, or sometimes an additional refining step. Gold from electronics is recovered with the non-Ferro fractions from WEEE and ELVs, and is returned to gold circuit via copper recycling.

B.3.3 Reconciled mass balances

These data represent the distribution of elements between the indicated phases of the unit operations relevant for processing as depicted by Figure B.16. These have been obtained by closing the mass balances by the use of data reconciliation techniques.

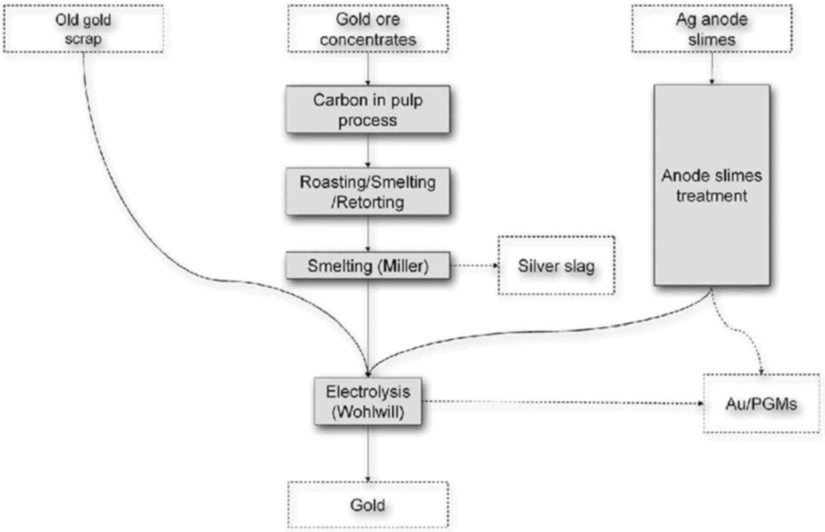


Figure B.16: Simplified gold production flowchart

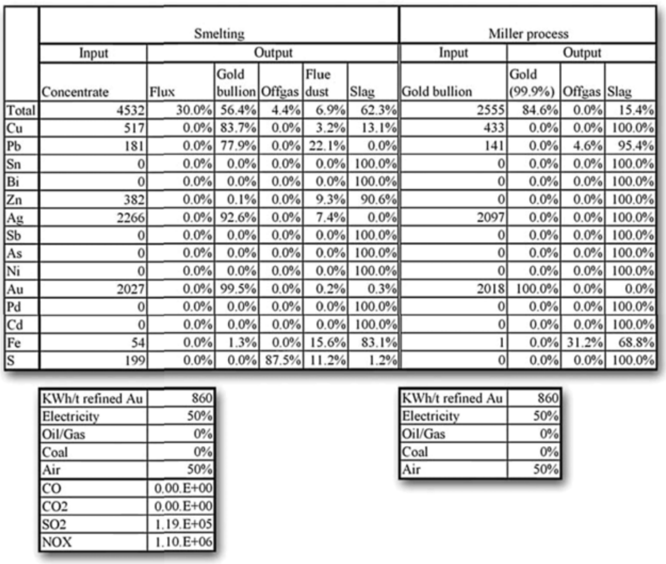
	Mining												
	Gravity concentration			Sulphide concentration			Carbon in leach process				
	Input	Output		Input	Output		Input			Output	
	Gold ore	Gravity conventrate	Tailings	Gold ore	Sulfide concentrate	Tailings	Gold ore	Gravity conventrate	Sulfide concentrate	Concentrate	Tailings
Total	3738700	14.4%	85.6%	5551800	8.0%	92.0%	49954042	540034	443923	0.0%	100.0%
Cu	0	0.0%	100.0%	0	0.0%	100.0%	0	0	0	0.0%	100.0%
Pb	0	0.0%	100.0%	0	0.0%	100.0%	0	0	0	0.0%	100.0%
Sn	0	0.0%	100.0%	0	0.0%	100.0%	0	0	0	0.0%	100.0%
Bi	0	0.0%	100.0%	0	0.0%	100.0%	0	0	0	0.0%	100.0%
Zn	0	0.0%	100.0%	0	0.0%	100.0%	0	0	0	0.0%	100.0%
Ag	0	0.0%	100.0%	0	0.0%	100.0%	0	0	0	0.0%	100.0%
Sb	0	0.0%	100.0%	0	0.0%	100.0%	0	0	0	0.0%	100.0%
As	0	0.0%	100.0%	1887600	84.7%	15.3%	0	0	1598114	0.0%	100.0%
Ni	0	0.0%	100.0%	0	0.0%	100.0%	0	0	0	0.0%	100.0%
Au	243	100.0%	0.0%	247	93.7%	6.3%	1678	243	231	94.0%	6.0%
Pd	0	0.0%	100.0%	0	0.0%	100.0%	0	0	0	0.0%	100.0%
Cd	0	0.0%	100.0%	0	0.0%	100.0%	0	0	0	0.0%	100.0%
Fe	0	0.0%	100.0%	0	0.0%	100.0%	0	0	0	0.0%	100.0%
S	0	0.0%	100.0%	9818000	100.0%	0.0%	0	0	9814780	0.0%	100.0%

KWh/t refined Au	860
Electricity	50%
Oil/Gas	0%
Coal	0%
Air	50%

KWh/t refined Au	860
Electricity	50%
Oil/Gas	0%
Coal	0%
Air	50%

KWh/t refined Au	860
Electricity	50%
Oil/Gas	0%
Coal	0%
Air	50%

Figure B.17: Data refers to recovery % in Mining in Figure B.16

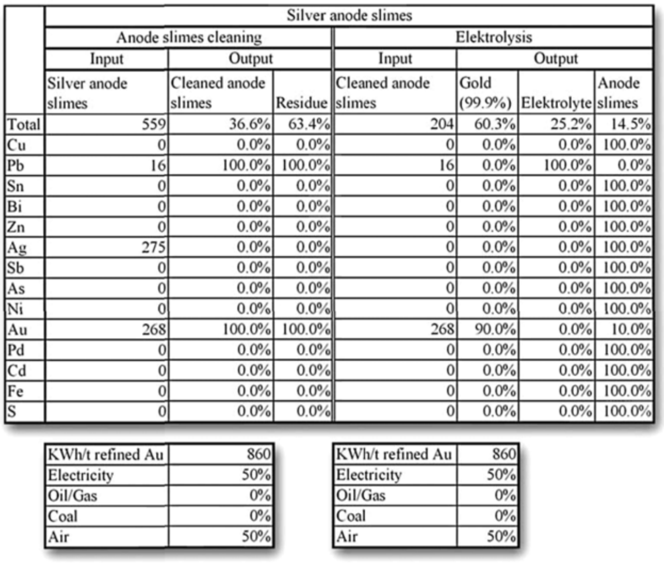


	Smelting						Miller process			
	Input	Output					Input	Output		
	Concentrate	Flux	Gold bullion	Offgas	Flue dust	Slag	Gold bullion	Gold (99.9%)	Offgas	Slag
Total	4532	30.0%	56.4%	4.4%	6.9%	62.3%	2555	84.6%	0.0%	15.4%
Cu	517	0.0%	83.7%	0.0%	3.2%	13.1%	433	0.0%	0.0%	100.0%
Pb	181	0.0%	77.9%	0.0%	22.1%	0.0%	141	0.0%	4.6%	95.4%
Sn	0	0.0%	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	100.0%
Bi	0	0.0%	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	100.0%
Zn	382	0.0%	0.1%	0.0%	9.3%	90.6%	0	0.0%	0.0%	100.0%
Ag	2266	0.0%	92.6%	0.0%	7.4%	0.0%	2097	0.0%	0.0%	100.0%
Sb	0	0.0%	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	100.0%
As	0	0.0%	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	100.0%
Ni	0	0.0%	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	100.0%
Au	2027	0.0%	99.5%	0.0%	0.2%	0.3%	2018	100.0%	0.0%	0.0%
Pd	0	0.0%	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	100.0%
Cd	0	0.0%	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	100.0%
Fe	54	0.0%	1.3%	0.0%	15.6%	83.1%	1	0.0%	31.2%	68.8%
S	199	0.0%	0.0%	87.5%	11.2%	1.2%	0	0.0%	0.0%	100.0%

KWh/t refined Au	860
Electricity	50%
Oil/Gas	0%
Coal	0%
Air	50%
CO	0.00.E+00
CO2	0.00.E+00
SO2	1.19.E+05
NOX	1.10.E+06

KWh/t refined Au	860
Electricity	50%
Oil/Gas	0%
Coal	0%
Air	50%

Figure B.18: Data refers to recovery % in Smelting and Miller processing in Figure B.16



	Silver anode slimes						
	Anode slimes cleaning			Elektrolysis			
	Input	Output		Input	Output		
	Silver anode slimes	Cleaned anode slimes	Residue	Cleaned anode slimes	Gold (99.9%)	Elektrolyte	Anode slimes
Total	559	36.6%	63.4%	204	60.3%	25.2%	14.5%
Cu	0	0.0%	0.0%	0	0.0%	0.0%	100.0%
Pb	16	100.0%	100.0%	16	0.0%	100.0%	0.0%
Sn	0	0.0%	0.0%	0	0.0%	0.0%	100.0%
Bi	0	0.0%	0.0%	0	0.0%	0.0%	100.0%
Zn	0	0.0%	0.0%	0	0.0%	0.0%	100.0%
Ag	275	0.0%	0.0%	0	0.0%	0.0%	100.0%
Sb	0	0.0%	0.0%	0	0.0%	0.0%	100.0%
As	0	0.0%	0.0%	0	0.0%	0.0%	100.0%
Ni	0	0.0%	0.0%	0	0.0%	0.0%	100.0%
Au	268	100.0%	100.0%	268	90.0%	0.0%	10.0%
Pd	0	0.0%	0.0%	0	0.0%	0.0%	100.0%
Cd	0	0.0%	0.0%	0	0.0%	0.0%	100.0%
Fe	0	0.0%	0.0%	0	0.0%	0.0%	100.0%
S	0	0.0%	0.0%	0	0.0%	0.0%	100.0%

KWh/t refined Au	860
Electricity	50%
Oil/Gas	0%
Coal	0%
Air	50%

KWh/t refined Au	860
Electricity	50%
Oil/Gas	0%
Coal	0%
Air	50%

Figure B.19: Data refers to recovery % from Silver Anode Slimes in Figure B.16

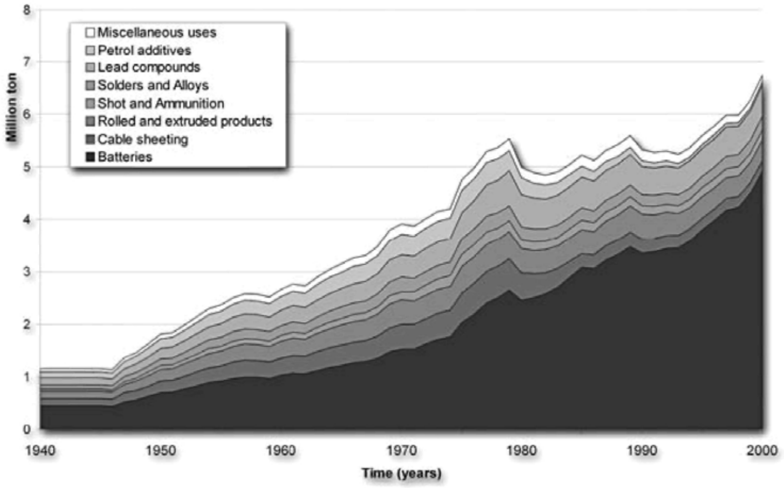


Figure B.20: Lead production and estimated end uses from 1940-2000 [227, 226]

B.4 Lead production and recycling profile

B.4.1 End uses

In 2000, about 6.65 million tons of lead was produced globally [227]. Lead has been used for centuries to make water pipes and to cover roofs. It is very easy to cast, and is extremely corrosion resistant. Lead pipes dating from Roman times are still in use [464]. In addition, lead is a good sound and radiation absorber and is attractive in its appearance. In past century, other uses for lead have been developed. Today, lead is used in a large number of applications as metallic lead in batteries and accumulators, lead shots, boat keels, building materials but also in products such as paint, leaded petrol, glass, electronic and electric equipment, plastic, ceramic products. Applications are being developed for lead and lead compounds in a number of new areas: microelectronics, superconductors, earthquake damping materials and radon gas shielding, and for retrievable storage or permanent disposal of nuclear waste, to name a few [220]. Major new applications are also being developed for traditional uses, notably lead-acid batteries, which are increasingly being used for emergency power applications, for powering electric and hybrid-electric vehicles and for energy storage in remote areas without access to electricity mains.

B.4.2 Production

Lead (typically 6%) is often found together with zinc (typically 9%), and copper (typically 0.5%) (other valuable elements associated with (zinc-)lead ores are silver, cadmium and bismuth). Some 20% of the lead is obtained form lead mines [470]. The zinc, lead and copper concentrates are separated at the mines, but considerable amounts of zinc can remain in the lead concentrate.

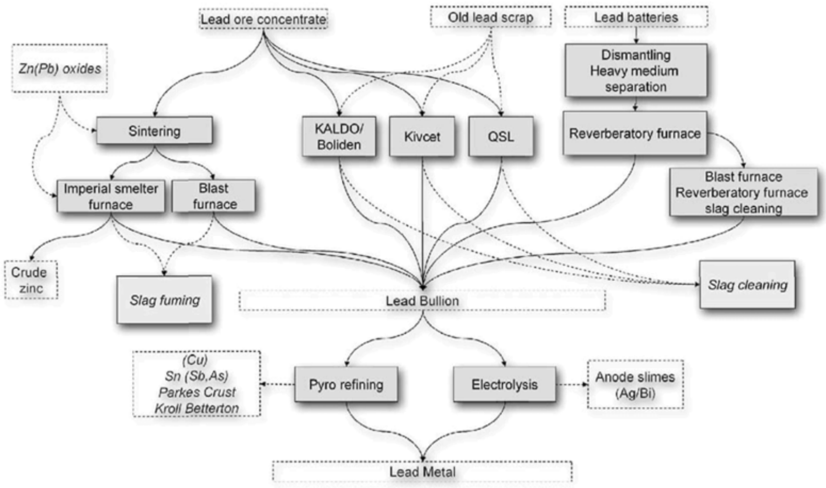


Figure B.21: Simplified lead production flowchart

This zinc is recovered from the lead smelting slags in zinc processes, or directly in the ISF process. After ore beneficiation, the lead concentrates typically contain 50-60% lead [466]. Lead production can be divided into two steps:

- Production of crude lead, the lead bullion, and
- refining of lead bullion to lead.

Secondary lead is processed as part of the feed to primary smelters, only the lead in lead-acid batteries is recovered in dedicated processes. Five most common furnaces for lead smelting are the blast furnace (52%), the Imperial Smelting furnace (24%), the QSL furnace (12%), the Kaldo Boliden furnace (7%) and the Kivcet furnace (5%) [471]. Traditionally, lead is produced with the blast furnace process or the imperial smelter process. Both processes use a sintering step to oxidize the sulphide concentrate and to obtain a lumpy and strong agglomerate suitable for use in the furnace. The Blast Furnace (BF) is the traditional metal production furnace. The furnace is a steel stack lined with refractory bricks, where sinter, coke and limestone are fed into the top in alternating layers. Preheated air is blown into the bottom. The sinter is reduced and the liquid reaction products are drained from the bottom of the furnace at regular intervals. The lead content of the sinter, mainly lead oxide is reduced to metallic lead. Other metal oxides present in the sinter, such as copper, antimony, arsenic and noble metals, are also reduced to their metallic state. Other constituents such as zinc and cadmium, report to the slag phase as oxides. If the zinc content of the slag is high, it is treated to remove the zinc. The Imperial Smelting Furnace (ISF) is similar to the Blast Furnace, but produces lead bullion and crude zinc simultaneously. The charge of the furnace is a mixed lead-zinc concentrate. The difference with the Blast Furnace is that the top of the furnace is closed to maintain a higher temperature in the top part of the furnace. As a consequence, the zinc remains as a gas, which is condensed in a lead metal bath, the spray condenser. The condensed, crude zinc needs is further refined by distillation (see the zinc profile). The flue dust production in the sintering step is a major environmental problem of the traditional routes. In order to avoid environmental problems, proper ventilation and dust cleaning equipment is required (e.g. Ullmann [466]). Modern smelting operations have been developed that apply direct smelting operations and avoid the sintering operation. The KIVCET, the QSL and the Kaldo processes are the most abundant examples of the new processes. The KIVCET furnace consists of two sectors; an oxidation section and a reduction section. In the oxidation section, the blended charge together with fluxes, recycle flue dust and oxygen are fed through burners. Combustion of the different charge products at a temperature of 1400°C results in almost a complete desulphurization before the reaction products collect in the slag bath. The lead monoxide from the charge combustion is reduced by a layer of floating coke particles on the slag bath under the combustion shaft. The reduced slag and the lead bullion flow to the reduction section where the remaining lead oxide is reduced and a slag with a typical lead content of 2-3% is produced. The Kivcet or KIVCET process can also smelt oxidic charge materials such as zinc leach residues [466]. The QSL furnace is a horizontal refractory lined vessel, which is divided into an oxidation section and a slag reduction section, similar to the KIVCET process. The input of the QSL process is a mixture of lead concentrate, fluxes, coal, flue dusts and other recycle streams. The oxidation products of the QSL process are a high lead slag, sulphur dioxide gas, flue dust and lead bullion. The Boliden Kaldo Process melting furnace is a top blown converter. A (batch) melting cycle starts with the combustion of the charge with oxygen in a preheated empty vessel. The combustion of the charge continues until the lead bullion and the high lead slag reach the top of the converter; from this point on the slag reduction starts. Lead sulphide concentrate is used recover a major portion of the lead monoxide produced in the oxygen charge combustion, followed by reduction with coke particles. The Boliden Kaldo process can handle a variety of scrap and recycling streams, such as flue dusts. The slags from all three processes can contain considerable amounts of zinc and lead. Depending on the lead and zinc content, they are either processed in zinc processes, or treated and recycled back to lead smelting. The lead bullion as produced in the melting operations still contains significant amounts of impurities, such as copper, arsenic, silver and bismuth, and needs to be refined. Worldwide, the two dominant lead refining operations are pyrometallurgical refining (72%) and electrorefining (28%) [471]. In the Pyrometallurgical Refining of lead impurities are separated into individual residue streams using batch processes:

- De-copperization,
- removal of arsenic, tin and antimony with the Harris process,
- removal of noble metals with Parkes process,
- dezincification and finally
- bismuth removal with the Kroll-Betterton process.

The Parkes crust is processed to recover silver and other precious metals; the Kroll-Betterton dross is processed to recover bismuth. In Electrorefining lead bullion is cast into anodes, which are dissolved in an electrolyte, typically a fluosilicate electrolyte. The lead is selectively precipitated on the cathode. Metals with a higher electrochemical potential than lead remain in solution, and accumulate in the anode slimes. These anode slimes are treated to recover the precious metals. Metals with a lower potential, such as iron, nickel and zinc, dissolve in the electrolyte, but will not deposit on the cathode. The main advantage of the pyrometallurgical lead refining is the sequential separation of impurities. In the electrorefining most impurities accumulate in the anode slimes and require complex separation processes for their recovery. Lead is the most recycled non-ferrous metal in the world. Production from recycled materials has risen steadily. It surpassed primary output for the first time in 1989. In 2000, about 60% of lead was produced from secondary material [227]. The steady growth of the amount of recycled lead is primarily due to its increased use in recyclable applications (in particular batteries) and a declining consumption for disperse uses such as leaded petrol. Also, general increases in the recycling rates of lead containing products such as vehicles and electrical and electronic equipment will result in increased secondary lead production. The main (old) scrap source for lead is batteries. Lamm [319] estimated that about 90-96% of the lead acid batteries are recovered. Before battery melting and producing lead bullion, the batteries are dismantled and mechanically separated using shredders and grinding mills, and the heavy medium separation. The metal fraction resulting from mechanical recycling is further processed in a reverberatory furnace producing lead bullion. The slag, still containing significant amounts of lead, is cleaned in either a single step, or in a two steps process, using reverberatory and blast furnaces. Battery recycling is a dedicated process; other lead containing products are recycled in the modern lead smelters such as the QSL, KIVCET and Kaldo furnaces. These other sources include lead dismantled during demolition wastes, and the old lead scrap, Ferro and non-Ferro fractions from the different waste recovery routes. The old lead scrap can be used directly in lead smelters, the Ferro fractions are typically recovered in electric arc furnaces in the iron production circuit. In the recycling of iron, lead, zinc and cadmium are recovered as flue dust. The electric arc furnace dust returns to the lead(-zinc) circuit by processing in Waelz kilns, or ISF processes. Whereas the ISF process produces lead bullion, the Waelz oxide must be further processed into lead bullion, in a Blast furnace for instance. Lead in the non-Ferro fractions can also be recovered.

B.4.3 Reconciled mass balances

These data represent the distribution of elements between the indicated phases of the unit operations relevant for processing as depicted by Figure B.21. These have been obtained by closing the mass balances by the use of data reconciliation techniques.

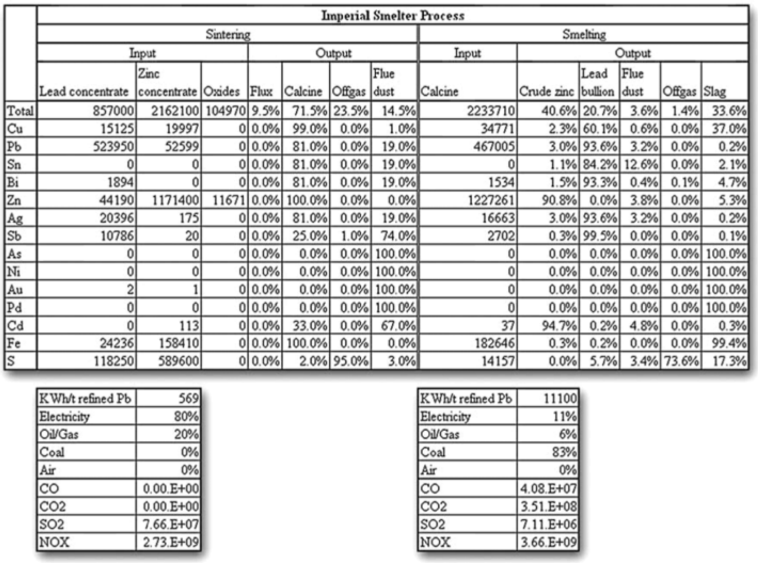
	Mining				
	Input	Output			
	Lead-zinc ore	Lead concentrate	Zinc concentrate	Copper concentrate	Tailings
Total	78778000	7.6%	13.8%	0.6%	78.0%
Cu	369850	28.6%	27.7%	26.5%	17.2%
Pb	4562100	81.0%	4.4%	0.8%	13.8%
Sn	0	0.0%	0.0%	0.0%	100.0%
Bi	0	0.0%	0.0%	0.0%	100.0%
Zn	6845000	4.4%	87.0%	0.3%	8.2%
Ag	6778	53.9%	13.9%	9.7%	22.4%
Sb	0	0.0%	0.0%	0.0%	100.0%
As	0	0.0%	0.0%	0.0%	100.0%
Ni	0	0.0%	0.0%	0.0%	100.0%
Au	47	22.5%	8.0%	4.1%	65.4%
Pd	0	0.0%	0.0%	0.0%	100.0%
Cd	0	0.0%	0.0%	0.0%	100.0%
Fe	10930000	3.1%	7.2%	0.0%	89.7%
S	16365000	5.1%	21.2%	0.9%	72.8%

KWh/t refined Pb	3752
Electricity	100%
Oil/Gas	0%
Coal	0%
Air	0%

	Slag cleaning			
	Input	Output		
	Slag	Fume	Offgas	Slag
Total	976180	15.6%	6.3%	78.1%
Cu	445	0.4%	0.0%	99.6%
Pb	20290	85.1%	0.0%	14.9%
Sn	395	4.3%	0.0%	95.7%
Bi	5	29.9%	0.0%	70.1%
Zn	84067	65.7%	0.0%	34.3%
Ag	6309	0.0%	0.0%	100.0%
Sb	164	100.0%	0.0%	0.0%
As	13	100.0%	0.0%	0.0%
Ni	0	0.0%	0.0%	100.0%
Au	3	0.0%	0.0%	100.0%
Pd	0	0.0%	0.0%	100.0%
Cd	0	0.0%	0.0%	100.0%
Fe	57749	2.9%	0.0%	97.1%
S	132	2.4%	96.6%	1.1%

KWh/t refined Pb	130
Electricity	50%
Oil/Gas	0%
Coal	0%
Air	50%
CO	0.00.E+00
CO2	0.00.E+00
SO2	8.69.E+04
NOX	8.09.E+05

Figure B.22: Data refers to Mining and Slag cleaning in Figure B.21

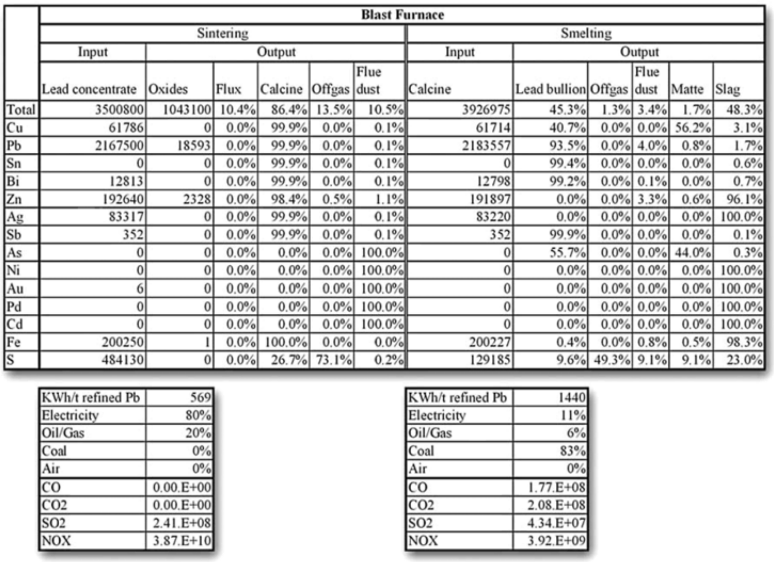


	Imperial Smelter Process												
	Sintering							Smelting					
	Input			Output				Input	Output				
	Lead concentrate	Zinc concentrate	Oxides	Flux	Calcine	Offgas	Flue dust	Calcine	Crude zinc	Lead bullion	Flue dust	Offgas	Slag
Total	857000	2162100	104970	9.5%	71.5%	23.5%	14.5%	2233710	40.6%	20.7%	3.6%	1.4%	33.6%
Cu	15125	19997	0	0.0%	99.0%	0.0%	1.0%	34771	2.3%	60.1%	0.6%	0.0%	37.0%
Pb	523950	52599	0	0.0%	81.0%	0.0%	19.0%	467005	3.0%	93.6%	3.2%	0.0%	0.2%
Sn	0	0	0	0.0%	81.0%	0.0%	19.0%	0	1.1%	84.2%	12.6%	0.0%	2.1%
Bi	1894	0	0	0.0%	81.0%	0.0%	19.0%	1534	1.5%	93.3%	0.4%	0.1%	4.7%
Zn	44190	1171400	11671	0.0%	100.0%	0.0%	0.0%	1227261	90.8%	0.0%	3.8%	0.0%	5.3%
Ag	20396	175	0	0.0%	81.0%	0.0%	19.0%	16663	3.0%	93.6%	3.2%	0.0%	0.2%
Sb	10786	20	0	0.0%	25.0%	1.0%	74.0%	2702	0.3%	99.5%	0.0%	0.0%	0.1%
As	0	0	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%
Ni	0	0	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%
Au	2	1	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%
Pd	0	0	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%
Cd	0	113	0	0.0%	33.0%	0.0%	67.0%	37	94.7%	0.2%	4.8%	0.0%	0.3%
Fe	24236	158410	0	0.0%	100.0%	0.0%	0.0%	182646	0.3%	0.2%	0.0%	0.0%	99.4%
S	118250	589600	0	0.0%	2.0%	95.0%	3.0%	14157	0.0%	5.7%	3.4%	73.6%	17.3%

KWh/t refined Pb	569
Electricity	80%
Oil/Gas	20%
Coal	0%
Air	0%
CO	0.00.E+00
CO2	0.00.E+00
SO2	7.66.E+07
NOX	2.73.E+09

KWh/t refined Pb	11100
Electricity	11%
Oil/Gas	6%
Coal	83%
Air	0%
CO	4.08.E+07
CO2	3.51.E+08
SO2	7.11.E+06
NOX	3.66.E+09

Figure B.23: Data refers to the recovery % in the Imperial Smelting Furnace in Figure B.21

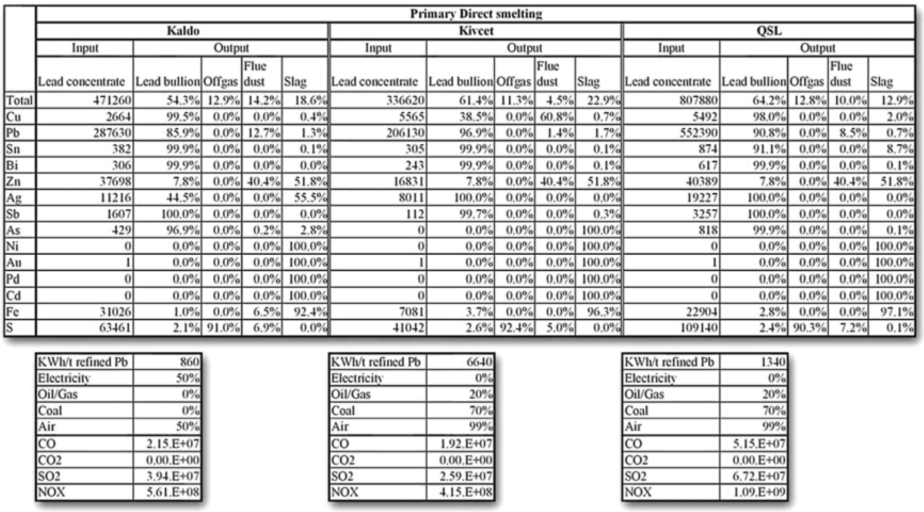


	Blast Furnace												
	Sintering						Smelting						
	Input	Output					Input	Output					
	Lead concentrate	Oxides	Flux	Calcine	Offgas	Flue dust	Calcine	Lead bullion	Offgas	Flue dust	Matte	Slag
Total	3500800	1043100	10.4%	86.4%	13.5%	10.5%	3926975	45.3%	1.3%	3.4%	1.7%	48.3%
Cu	61786	0	0.0%	99.9%	0.0%	0.1%	61714	40.7%	0.0%	0.0%	56.2%	3.1%
Pb	2167500	18593	0.0%	99.9%	0.0%	0.1%	2183557	93.5%	0.0%	4.0%	0.8%	1.7%
Sn	0	0	0.0%	99.9%	0.0%	0.1%	0	99.4%	0.0%	0.0%	0.0%	0.6%
Bi	12813	0	0.0%	99.9%	0.0%	0.1%	12798	99.2%	0.0%	0.1%	0.0%	0.7%
Zn	192640	2328	0.0%	98.4%	0.5%	1.1%	191897	0.0%	0.0%	3.3%	0.6%	96.1%
Ag	83317	0	0.0%	99.9%	0.0%	0.1%	83220	0.0%	0.0%	0.0%	0.0%	100.0%
Sb	352	0	0.0%	99.9%	0.0%	0.1%	352	99.9%	0.0%	0.0%	0.0%	0.1%
As	0	0	0.0%	0.0%	0.0%	100.0%	0	55.7%	0.0%	0.0%	44.0%	0.3%
Ni	0	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%
Au	6	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%
Pd	0	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%
Cd	0	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%
Fe	200250	1	0.0%	100.0%	0.0%	0.0%	200227	0.4%	0.0%	0.8%	0.5%	98.3%
S	484130	0	0.0%	26.7%	73.1%	0.2%	129185	9.6%	49.3%	9.1%	9.1%	23.0%

KWh/t refined Pb	569
Electricity	80%
Oil/Gas	20%
Coal	0%
Air	0%
CO	0.00.E+00
CO2	0.00.E+00
SO2	2.41.E+08
NOX	3.87.E+10

KWh/t refined Pb	1440
Electricity	11%
Oil/Gas	6%
Coal	83%
Air	0%
CO	1.77.E+08
CO2	2.08.E+08
SO2	4.34.E+07
NOX	3.92.E+09

Figure B.24: Data refers to recovery % in the Blast furnace in Figure B.21



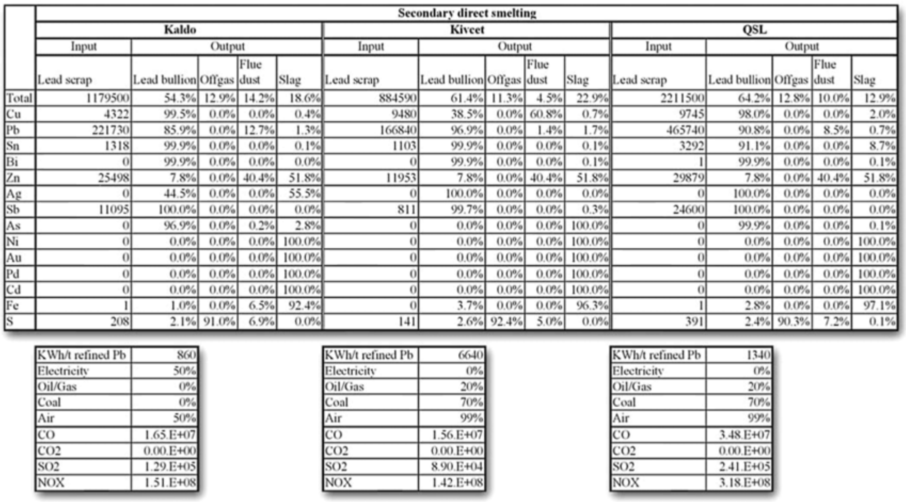
	Primary Direct smelting														
	Kaldo					Kivcet					QSL				
	Input	Output				Input	Output				Input	Output			
	Lead concentrate	Lead bullion	Offgas	Flue dust	Slag	Lead concentrate	Lead bullion	Offgas	Flue dust	Slag	Lead concentrate	Lead bullion	Offgas	Flue dust	Slag
Total	471260	54.3%	12.9%	14.2%	18.6%	336620	61.4%	11.3%	4.5%	22.9%	807880	64.2%	12.8%	10.0%	12.9%
Cu	2664	99.5%	0.0%	0.0%	0.4%	5565	38.5%	0.0%	60.8%	0.7%	5492	98.0%	0.0%	0.0%	2.0%
Pb	287630	85.9%	0.0%	12.7%	1.3%	206130	96.9%	0.0%	1.4%	1.7%	552390	90.8%	0.0%	8.5%	0.7%
Sn	382	99.9%	0.0%	0.0%	0.1%	305	99.9%	0.0%	0.0%	0.1%	874	91.1%	0.0%	0.0%	8.7%
Bi	306	99.9%	0.0%	0.0%	0.0%	243	99.9%	0.0%	0.0%	0.1%	617	99.9%	0.0%	0.0%	0.1%
Zn	37698	7.8%	0.0%	40.4%	51.8%	16831	7.8%	0.0%	40.4%	51.8%	40389	7.8%	0.0%	40.4%	51.8%
Ag	11216	44.5%	0.0%	0.0%	55.5%	8011	100.0%	0.0%	0.0%	0.0%	19227	100.0%	0.0%	0.0%	0.0%
Sb	1607	100.0%	0.0%	0.0%	0.0%	112	99.7%	0.0%	0.0%	0.3%	3257	100.0%	0.0%	0.0%	0.0%
As	429	96.9%	0.0%	0.2%	2.8%	0	0.0%	0.0%	0.0%	100.0%	818	99.9%	0.0%	0.0%	0.1%
Ni	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	100.0%
Au	1	0.0%	0.0%	0.0%	100.0%	1	0.0%	0.0%	0.0%	100.0%	1	0.0%	0.0%	0.0%	100.0%
Pd	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	100.0%
Cd	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	100.0%
Fe	31026	1.0%	0.0%	6.5%	92.4%	7081	3.7%	0.0%	0.0%	96.3%	22904	2.8%	0.0%	0.0%	97.1%
S	63461	2.1%	91.0%	6.9%	0.0%	41042	2.6%	92.4%	5.0%	0.0%	109140	2.4%	90.3%	7.2%	0.1%

KWh/t refined Pb	860
Electricity	50%
Oil/Gas	0%
Coal	0%
Air	50%
CO	2.15.E+07
CO2	0.00.E+00
SO2	3.94.E+07
NOX	5.61.E+08

KWh/t refined Pb	6640
Electricity	0%
Oil/Gas	20%
Coal	70%
Air	99%
CO	1.92.E+07
CO2	0.00.E+00
SO2	2.59.E+07
NOX	4.15.E+08

KWh/t refined Pb	1340
Electricity	0%
Oil/Gas	20%
Coal	70%
Air	99%
CO	5.15.E+07
CO2	0.00.E+00
SO2	6.72.E+07
NOX	1.09.E+09

Figure B.25: Data refers to the recovery % in primary direct smelting processes in Figure B.21



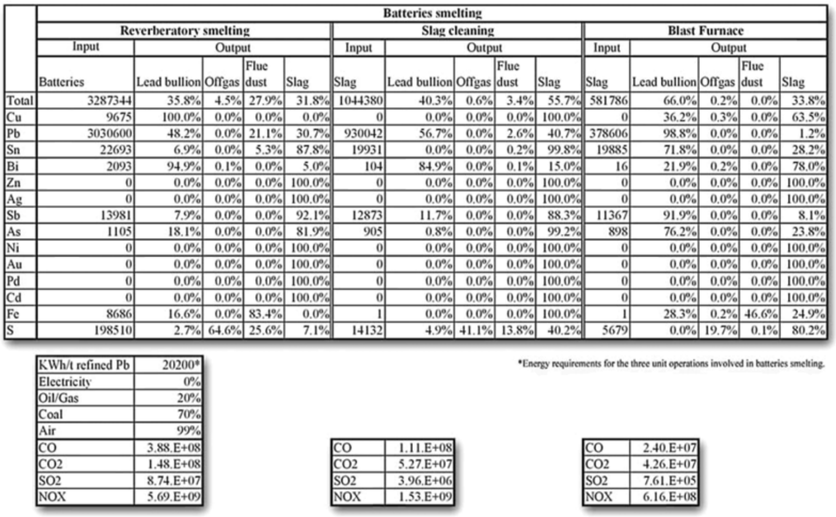
	Secondary direct smelting														
	Kaldo					Kivcet					QSL				
	Input	Output				Input	Output				Input	Output			
	Lead scrap	Lead bullion	Offgas	Flue dust	Slag	Lead scrap	Lead bullion	Offgas	Flue dust	Slag	Lead scrap	Lead bullion	Offgas	Flue dust	Slag
Total	1179500	54.3%	12.9%	14.2%	18.6%	884590	61.4%	11.3%	4.5%	22.9%	2211500	64.2%	12.8%	10.0%	12.9%
Cu	4322	99.5%	0.0%	0.0%	0.4%	9480	38.5%	0.0%	60.8%	0.7%	9745	98.0%	0.0%	0.0%	2.0%
Pb	221730	85.9%	0.0%	12.7%	1.3%	166840	96.9%	0.0%	1.4%	1.7%	465740	90.8%	0.0%	8.5%	0.7%
Sn	1318	99.9%	0.0%	0.0%	0.1%	1103	99.9%	0.0%	0.0%	0.1%	3292	91.1%	0.0%	0.0%	8.7%
Bi	0	99.9%	0.0%	0.0%	0.0%	0	99.9%	0.0%	0.0%	0.1%	1	99.9%	0.0%	0.0%	0.1%
Zn	25498	7.8%	0.0%	40.4%	51.8%	11953	7.8%	0.0%	40.4%	51.8%	29879	7.8%	0.0%	40.4%	51.8%
Ag	0	44.5%	0.0%	0.0%	55.5%	0	100.0%	0.0%	0.0%	0.0%	0	100.0%	0.0%	0.0%	0.0%
Sb	11095	100.0%	0.0%	0.0%	0.0%	811	99.7%	0.0%	0.0%	0.3%	24600	100.0%	0.0%	0.0%	0.0%
As	0	96.9%	0.0%	0.2%	2.8%	0	0.0%	0.0%	0.0%	100.0%	0	99.9%	0.0%	0.0%	0.1%
Ni	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	100.0%
Au	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	100.0%
Pd	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	100.0%
Cd	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	100.0%
Fe	1	1.0%	0.0%	6.5%	92.4%	0	3.7%	0.0%	0.0%	96.3%	1	2.8%	0.0%	0.0%	97.1%
S	208	2.1%	91.0%	6.9%	0.0%	141	2.6%	92.4%	5.0%	0.0%	391	2.4%	90.3%	7.2%	0.1%

KWh/t refined Pb	860
Electricity	50%
Oil/Gas	0%
Coal	0%
Air	50%
CO	1.65.E+07
CO2	0.00.E+00
SO2	1.29.E+05
NOX	1.51.E+08

KWh/t refined Pb	6640
Electricity	0%
Oil/Gas	20%
Coal	70%
Air	99%
CO	1.56.E+07
CO2	0.00.E+00
SO2	8.90.E+04
NOX	1.42.E+08

KWh/t refined Pb	1340
Electricity	0%
Oil/Gas	20%
Coal	70%
Air	99%
CO	3.48.E+07
CO2	0.00.E+00
SO2	2.41.E+05
NOX	3.18.E+08

Figure B.26: Data refers to recovery % in secondary direct smelting processes in Figure B.21



	Batteries smelting														
	Reverberatory smelting					Slag cleaning					Blast Furnace				
	Input	Output				Input	Output				Input	Output			
	Batteries	Lead bullion	Offgas	Flue dust	Slag	Slag	Lead bullion	Offgas	Flue dust	Slag	Slag	Lead bullion	Offgas	Flue dust	Slag
Total	3287344	35.8%	4.5%	27.9%	31.8%	1044380	40.3%	0.6%	3.4%	55.7%	581786	66.0%	0.2%	0.0%	33.8%
Cu	9675	100.0%	0.0%	0.0%	0.0%	0	0.0%	0.0%	0.0%	100.0%	0	36.2%	0.3%	0.0%	63.5%
Pb	3030600	48.2%	0.0%	21.1%	30.7%	930042	56.7%	0.0%	2.6%	40.7%	378606	98.8%	0.0%	0.0%	1.2%
Sn	22693	6.9%	0.0%	5.3%	87.8%	19931	0.0%	0.0%	0.2%	99.8%	19885	71.8%	0.0%	0.0%	28.2%
Bi	2093	94.9%	0.1%	0.0%	5.0%	104	84.9%	0.0%	0.1%	15.0%	16	21.9%	0.2%	0.0%	78.0%
Zn	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	100.0%
Ag	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	100.0%
Sb	13981	7.9%	0.0%	0.0%	92.1%	12873	11.7%	0.0%	0.0%	88.3%	11367	91.9%	0.0%	0.0%	8.1%
As	1105	18.1%	0.0%	0.0%	81.9%	905	0.8%	0.0%	0.0%	99.2%	898	76.2%	0.0%	0.0%	23.8%
Ni	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	100.0%
Au	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	100.0%
Pd	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	100.0%
Cd	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	100.0%
Fe	8686	16.6%	0.0%	83.4%	0.0%	1	0.0%	0.0%	0.0%	100.0%	1	28.3%	0.2%	46.6%	24.9%
S	198510	2.7%	64.6%	25.6%	7.1%	14132	4.9%	41.1%	13.8%	40.2%	5679	0.0%	19.7%	0.1%	80.2%

KWh/t refined Pb	20200*
Electricity	0%
Oil/Gas	20%
Coal	70%
Air	99%
CO	3.88.E+08
CO2	1.48.E+08
SO2	8.74.E+07
NOX	5.69.E+09

CO	1.11.E+08
CO2	5.27.E+07
SO2	3.96.E+06
NOX	1.53.E+09

CO	2.40.E+07
CO2	4.26.E+07
SO2	7.61.E+05
NOX	6.16.E+08

*Energy requirements for the three unit operations involved in batteries smelting.

Figure B.27: Data refers to recovery % in batteries smelting in Figure B.21

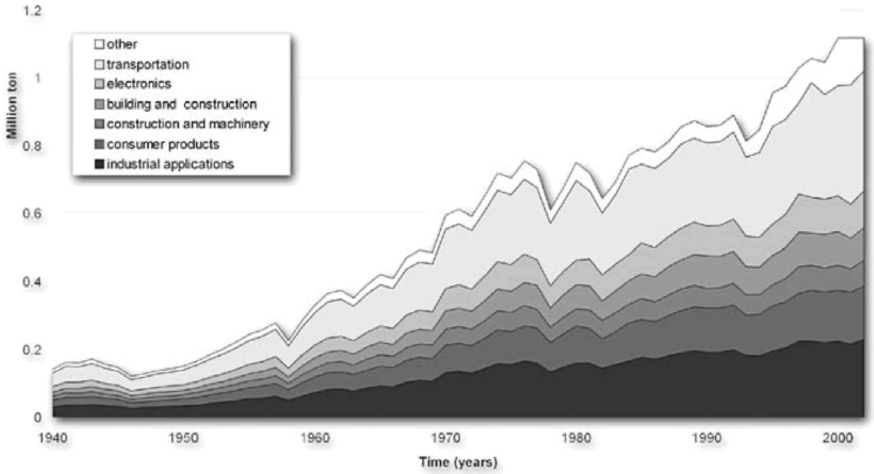


Figure B.28: Nickel production and estimated end uses from 1940-2000 [227, 146, 226]

B.5 Nickel production and recycling profile

B.5.1 End uses

In 2000 globally about 1.12 millions tons were produced [227]. Nickel is produced as nickel metal (ca. 56-64%), as nickel oxide (ca. 10-18%) and as ferronickel (ca. 22%)[3]. Nearly 90% of all nickel is consumed in the production of different stainless and alloy steels, other nickel alloys and foundry products. The steels and other nickel alloys are processed into commercial products in a number of industrial applications. These applications include building and construction materials; chemicals production; process equipment; petroleum refining, power generation, and other industrial processes components and machinery; automotive, railway, marine, aerospace, and other transportation equipment; electronics; and consumer and other products. About 9% is used in plated products, and the remaining two percent is used in a number of other relatively small applications, including chemicals, catalysts, batteries, coins, pigments, and powders (including powder metallurgy).

B.5.2 Production

The complex metallurgy of producing nickel from these ores is reflected in the wide range of extraction and refining processes in operation. Nickel is produced from both sulphide (86%) and oxide (14%) ores[4], that both have different production routes (Figure B.29). Nickel sulphides are often found together with economically recoverable amounts of copper, cobalt, gold, silver, platinum group metals and several other metals. The nickel content of sulphide

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[3] These data are 1998 estimates from Norilsk Nickel (`WWW.nornik.ru`) as used in the Ecobalance [472]

[4] These data vary in literature, for instance the NF BREF [473] about 60% of the nickel comes from sulphide deposits and 40% from oxide deposits.

ores usually can be concentrated several times (up to 25% Ni) by the relatively economical ore dressing techniques before the concentrate is smelted and refined to nickel products [473]. Oxidic ores, in contrast, are amenable to only limited beneficiation by physical methods e.g. magnetic or heavy media techniques, and therefore almost the entire volume of ore must go directly to metallurgical plants. Thus, oxidic processing tends to be more cost intensive, but mining costs are usually much lower than for sulphide ores. These differences, plus the availability of by-product value, can have an important influence on the viability of a specific deposit and whether refined metal or Ferro-nickel is produced from it: Most oxidic ores are used for the production of ferronickel. The production of nickel from sulphide ores can be divided into two steps:

- Smelting and converting the sulphide ore to matte that contains 35-70% Ni
- processing the matte to nickel.

The treatment of sulphide ores is similar to the treatment of copper sulphides. The process can be divided into three steps, viz. roasting, smelting and converting. In the roasting step, sulphur and iron are partly oxidized. In the smelting step, the roasting product is smelted together with a siliceous flux to produce two immiscible phases: An iron-silicate slag and a matte containing mainly nickel and copper sulphides. The last step is to convert the matte into a high-grade nickel copper matte by oxidation, sulphide is driven off as sulphur dioxide and the remaining iron is oxidized and removed in a silicate slag. If the slag contains high amounts of nickel or copper, the slag can be treated to recover the nickel and copper. In most of the modern operations the roasting step has been eliminated, the concentrate is fed directly into the smelter. Globally three furnaces are used to convert the sulphide ore into matte: The reverberatory (14%), electric (56%) and (Outokumpu and INCO) flash smelting furnace (30%). In Europe, only the Outokumpu flash furnace is used [473]. As nickel smelting is similar to copper smelting, the operation of these furnaces is more or less the same as in copper production. Both flash furnaces were initially developed for the treatment of copper concentrates. (The concentrates are roasted and melted in suspension in the furnace and fall into the settler in the same manner. The Inco furnace use commercial oxygen, however, while the Outokumpu furnace uses oxygen enriched air.) The reverberatory furnace is a long rectangular structure with an arched roof. The burners are located at one end in the roof. The charge is fed through pipes mounted on the roof along the side of the furnace. As an additional charge, molten converter slag can be introduced into the furnace. As the charge melts, it flows to the centre. The matte is tapped from the side; the slag is tapped from the end opposite to the burners. Fossil fuel is burned separately from the material that is being smelted. The reverberatory furnace has low energy efficiency, because the off gas stream carries nearly 50% of the heating value of the fuel. In the electric furnace electric energy is the heating source and is used if the cost of electric energy is low. The electric furnace is heated by passing a three-way current through a circuit consisting of carbon electrodes immersed in the slag. The concentrate and flux are charged from the top. As there is no fuel combustion, the quantity of off gas is much smaller compared to the reverberatory furnace, and heat and dust recovery is easier. In a flash smelting furnace, the process heat is supplied by (partial) oxidation of the sulphur and iron in the charge. In the current practice, which uses oxygen-enriched air, the process is autogenous. This process usually generates less off gas and is more energy efficient than the other two processes. The subsequent matte converting is usually performed in a Peirce-Smith converter, a horizontal side blown converter. Air or oxygen-enriched air is blown through the matte to oxidize the iron and remove some of the sulphur. The iron oxides are "slagged off" through the addition of silica fluxes. The matte is a melt of nickel (50-60%) and copper sulphides with small amounts of cobalt sulphides, iron, precious metals and other impurities. Because nickel in many applications is used as an alloying element, highly refined metals are not necessary for these applications; in other applications, high purity nickel is essential and the matte must be refined [166]. The object of the refining process is not only to remove the impurities form the nickel, but also to recover those that have economic value (e.g. copper and PGMs). There are six different processes to treat nickel matte: Hydrochloric Acid Leach, Atmospheric Acid Leach, Acid Pressure Leach, Ammonia Pressure Leach, Direct Electrolysis and Matte Separation. In addition to nickel matte, nickel ore, or nickel products from other operations are used as feed as well. Which process is used depends on the characteristics of the nickel matte, most importantly the copper and sulphur content of the matte. In the matte separation process (19%), the matte is slowly cooled. The matte segregates into three phases during cooling: a copper sulphide (Cu_2S) phase, a nickel sulphide (Ni_3S_2) phase and a nickel-copper alloy phase. Precious metals will collect in the latter phase. After solidification, the three phases are crushed and ground and are separated by magnetic separation and flotation. The nickel-copper alloy is refined using the carbonyl process, in which nickel is separated from the impurities using carbon monoxide. Under the process condition only Ni volatilizes as $Ni(CO)_4$. As other metals do not react with the carbon monoxide, or react at a much lower pace, this produces a very pure nickel. The nickel sulphide is roasted to nickel oxide in a fluidized bed roaster. Alternatively, the matte can leached to dissolve the nickel. The nickel in the leach solutions is recovered by electrolysis. Globally, four different leach processes are employed to leach the nickel matte. In the ammonia leach process (20%) matte is leached in a two-stage counter current process. Nickel, copper and cobalt form complexes with ammonia and are dissolved. The atmospheric acid leach process (11%) treats high copper, low sulphur nickel matte. In the process leaching is carried out in trains of air agitated Pachuca tanks. The acid pressure leach process (11%) is also used for nickel mattes that contain high concentrations of copper. The process is carried out in horizontal multi-compartment autoclaves and allows very high extractions of nickel, copper and sulphur. In addition, it can also be employed to extract PGMs from the matte, and is used by the platinum producers in South Africa for this reason. The PGMs are concentrated in the leach residue, producing a high-grade PGM concentrate (dependent on the feed). The concentrate can be directly treated in a platinum refinery. In the chloride leaching process (18%), the matte is leached under atmospheric pressure at the boiling point of the leach solution. In case the matte contains low concentrations of copper, the leaching step can be skipped. In this direct electrolysis process (21%), the matte is cast into anodes; the nickel is dissolved in the sulphate electrolyte and deposited on the cathode. The precious metals do not dissolve and will collect in the anode slimes. This process is mainly used by the Russian PGM producers.

Oxide nickel ores typically contain large amounts of iron, and small amounts of copper. The oxide ores can be processed hydrometallurgically into nickel, or pyrometallurgically into ferronickel or nickel matte. The nickel matte is treated analogous to the matte from sulphide ores. Oxide ores are more abundant and easier to extract than sulphide ores, however the energy requirements for oxide ore processes are much higher than for sulphide ore processes. Three pyrometallurgical processes exist to treat the oxide ores. In the rotary kiln - electric furnace process (48%) the ore is dried and partial reduced in a rotary kiln at temperatures of 900-1000°C; as fuel coal or coke is used. The produced calcine is fed into an electric furnace and heated to 1400-1650°C. Dependent on the magnesia and silica content of the ore flux is added. The carbon electrodes that are submerged into the slag layer reduce the nickel and iron oxides to metals. The Falcondo process (8%) is a process similar to the rotary kiln-electric arc furnace process, the calcination of the ore however is done with a shaft furnace instead

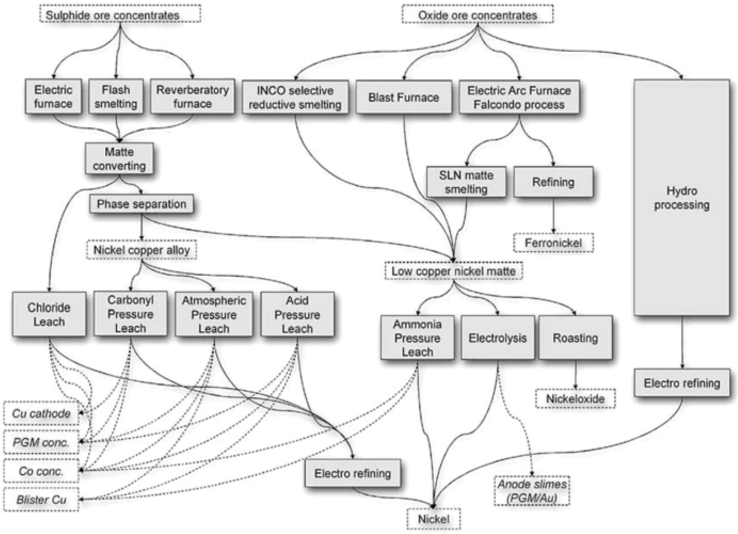
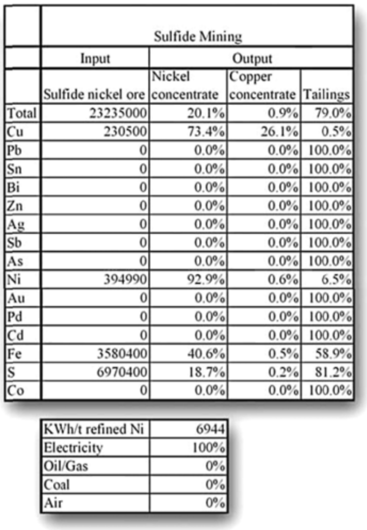


Figure B.29: Simplified nickel production flowchart of a rotary kiln. This process has a lower energy consumption compared to the common route to produce ferronickel; this is only possible due to the special composition of the ore. Virtually all nickel and approximately 65% of the iron are reduced to metal producing a crude ferronickel. The crude ferronickel is further refined in a similar way as steel refining: First the ferronickel is treated under reducing conditions to remove the sulphur, then refined under oxidizing conditions with suitable fluxes to remove carbon, silicon and phosphorous. The ferronickel is used to produce stainless steel. Ferronickel can also be converted to nickel matte using the SLN matte converting process. In this process, the ferronickel is converted into a matte by mixing it with elemental sulphur in a Peirce-Smith converter. After "sulphidizing" the matte is blown with air in order to oxidize the iron. In the blast furnace (or shaft furnace, 5%) oxide ore is converted to nickel matte. The ore is blended with coke, limestone and pyrite and sintered in a sinter machine. The resulting sinter is smelted in the furnace using oxygen-enriched air to produce furnace matte. This matte is blown in a Peirce-Smith converter to a high-grade converter matte. In the Inco selective reduction smelting process (26%) oxide ores are directly converted into nickel matte. The ore is first dried and partially reduced in a rotary kiln by adding coal and high sulphur oil into the ore bed. The hot calcine is smelted in an electric furnace. To produce the matte elemental sulphur is added. The resulting matte is further upgraded in an air blown converter. Finally, nickel can be produced from oxide ores in two hydrometallurgical processes: The Moa bay process and the Caron process (13%). In the Caron process, partially reduced ore is leached in ammoniacal solution. The Moa Bay process applies a direct sulphuric acid pressure leach. The main source of secondary nickel is stainless steel. This is usually remelted and refined to produce new stainless steel [466]. It is estimated that around 80 per cent of the nickel is recycled from new and old stainless steel scrap and returns to that end use [473]. Other nickel bearing materials (e.g. electronics, precipitates and residues) are recycled to primary production through production processes of other metals. Industrial applications, construction and machinery applications, large transportation applications (aerospace and marine) and the "other" applications are assumed to be recovered through other routes.

B.5.3 Reconciled mass balances

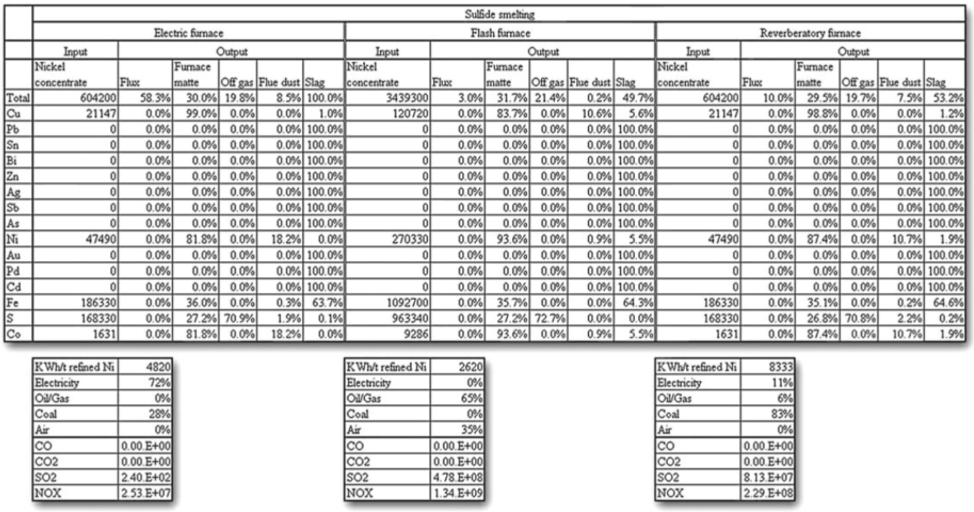
These data represent the distribution of elements between the indicated phases of the unit operations relevant for processing as depicted by Figure B.29. These have been obtained by closing the mass balances by the use of data reconciliation techniques.



	Sulfide Mining			
	Input	Output		
	Sulfide nickel ore	Nickel concentrate	Copper concentrate	Tailings
Total	23235000	20.1%	0.9%	79.0%
Cu	230500	73.4%	26.1%	0.5%
Pb	0	0.0%	0.0%	100.0%
Sn	0	0.0%	0.0%	100.0%
Bi	0	0.0%	0.0%	100.0%
Zn	0	0.0%	0.0%	100.0%
Ag	0	0.0%	0.0%	100.0%
Sb	0	0.0%	0.0%	100.0%
As	0	0.0%	0.0%	100.0%
Ni	394990	92.9%	0.6%	6.5%
Au	0	0.0%	0.0%	100.0%
Pd	0	0.0%	0.0%	100.0%
Cd	0	0.0%	0.0%	100.0%
Fe	3580400	40.6%	0.5%	58.9%
S	6970400	18.7%	0.2%	81.2%
Co	0	0.0%	0.0%	100.0%

KWh/t refined Ni	6944
Electricity	100%
Oil/Gas	0%
Coal	0%
Air	0%

Figure B.30: Data refers to Mining in Figure B.29



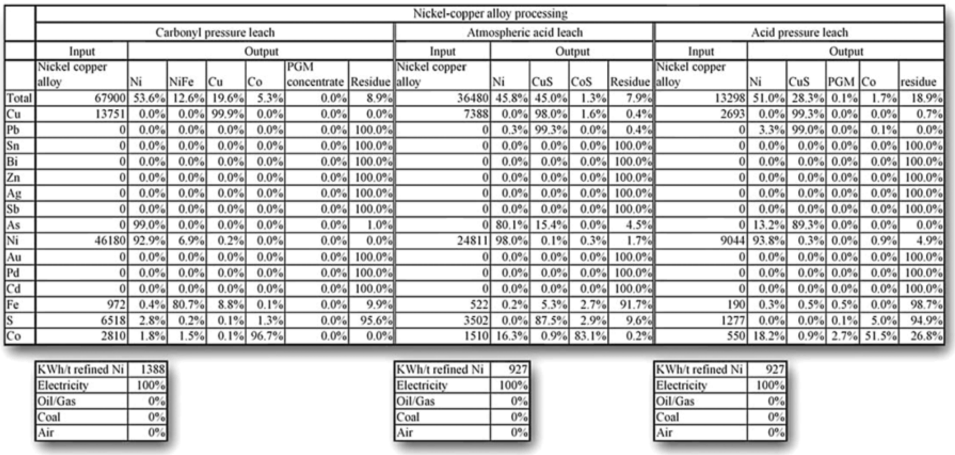
	Sulfide smelting																	
	Electric furnace						Flash furnace						Reverberatory furnace					
	Input	Output					Input	Output					Input	Output				
	Nickel concentrate	Flux	Furnace matte	Off gas	Flue dust	Slag	Nickel concentrate	Flux	Furnace matte	Off gas	Flue dust	Slag	Nickel concentrate	Flux	Furnace matte	Off gas	Flue dust	Slag
Total	604200	58.3%	30.0%	19.8%	8.5%	100.0%	3439300	3.0%	31.7%	21.4%	0.2%	49.7%	604200	10.0%	29.5%	19.7%	7.5%	53.2%
Cu	21147	0.0%	99.0%	0.0%	0.0%	1.0%	120720	0.0%	83.7%	0.0%	10.6%	5.6%	21147	0.0%	98.8%	0.0%	0.0%	1.2%
Pb	0	0.0%	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%
Sn	0	0.0%	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%
Bi	0	0.0%	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%
Zn	0	0.0%	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%
Ag	0	0.0%	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%
Sb	0	0.0%	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%
As	0	0.0%	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%
Ni	47490	0.0%	81.8%	0.0%	18.2%	0.0%	270330	0.0%	93.6%	0.0%	0.9%	5.5%	47490	0.0%	87.4%	0.0%	10.7%	1.9%
Au	0	0.0%	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%
Pd	0	0.0%	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%
Cd	0	0.0%	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%
Fe	186330	0.0%	36.0%	0.0%	0.3%	63.7%	1092700	0.0%	35.7%	0.0%	0.0%	64.3%	186330	0.0%	35.1%	0.0%	0.2%	64.6%
S	168330	0.0%	27.2%	70.9%	1.9%	0.1%	963340	0.0%	27.2%	72.7%	0.0%	0.0%	168330	0.0%	26.8%	70.8%	2.2%	0.2%
Co	1631	0.0%	81.8%	0.0%	18.2%	0.0%	9286	0.0%	93.6%	0.0%	0.9%	5.5%	1631	0.0%	87.4%	0.0%	10.7%	1.9%

KWh/t refined Ni	4820
Electricity	72%
Oil/Gas	0%
Coal	28%
Air	0%
CO	0.00.E+00
CO2	0.00.E+00
SO2	2.40.E+02
NOX	2.53.E+07

KWh/t refined Ni	2620
Electricity	0%
Oil/Gas	65%
Coal	0%
Air	35%
CO	0.00.E+00
CO2	0.00.E+00
SO2	4.78.E+08
NOX	1.34.E+09

KWh/t refined Ni	8333
Electricity	11%
Oil/Gas	6%
Coal	83%
Air	0%
CO	0.00.E+00
CO2	0.00.E+00
SO2	8.13.E+07
NOX	2.29.E+08

Figure B.31: Data refers to recovery % in Sulphide Smelting in Figure B.29



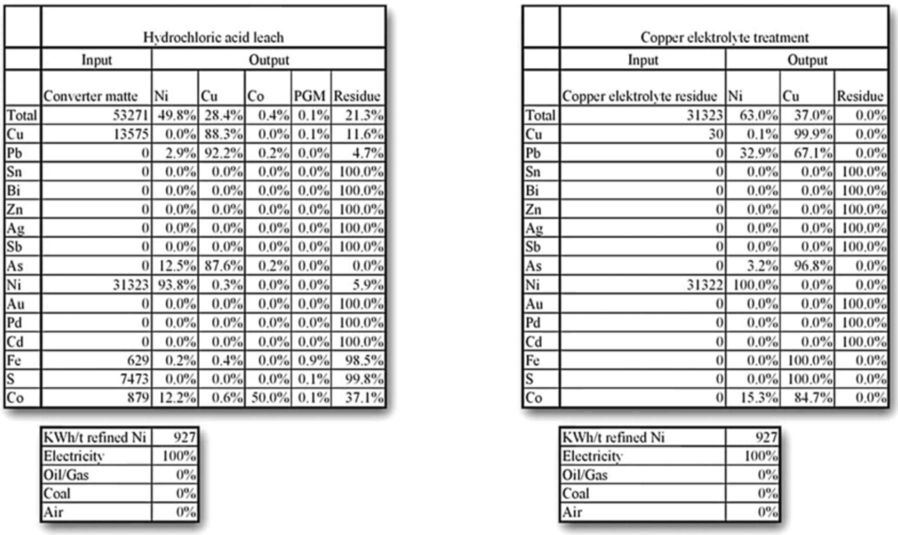
	Nickel-copper alloy processing																	
	Carbonyl pressure leach							Atmospheric acid leach					Acid pressure leach					
	Input	Output						Input	Output				Input	Output				
	Nickel copper alloy	Ni	NiFe	Cu	Co	PGM concentrate	Residue	Nickel copper alloy	Ni	CuS	CoS	Residue	Nickel copper alloy	Ni	CuS	PGM	Co	residue
Total	67900	53.6%	12.6%	19.6%	5.3%	0.0%	8.9%	36480	45.8%	45.0%	1.3%	7.9%	13298	51.0%	28.3%	0.1%	1.7%	18.9%
Cu	13751	0.0%	0.0%	99.9%	0.0%	0.0%	0.0%	7388	0.0%	98.0%	1.6%	0.4%	2693	0.0%	99.3%	0.0%	0.0%	0.7%
Pb	0	0.0%	0.0%	0.0%	0.0%	0.0%	100.0%	0	0.3%	99.3%	0.0%	0.4%	0	3.3%	99.0%	0.0%	0.1%	0.0%
Sn	0	0.0%	0.0%	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%
Bi	0	0.0%	0.0%	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%
Zn	0	0.0%	0.0%	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%
Ag	0	0.0%	0.0%	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%
Sb	0	0.0%	0.0%	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%
As	0	99.0%	0.0%	0.0%	0.0%	0.0%	1.0%	0	80.1%	15.4%	0.0%	4.5%	0	13.2%	89.3%	0.0%	0.0%	0.0%
Ni	46180	92.9%	6.9%	0.2%	0.0%	0.0%	0.0%	24811	98.0%	0.1%	0.3%	1.7%	9044	93.8%	0.3%	0.0%	0.9%	4.9%
Au	0	0.0%	0.0%	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%
Pd	0	0.0%	0.0%	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%
Cd	0	0.0%	0.0%	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%
Fe	972	0.4%	80.7%	8.8%	0.1%	0.0%	9.9%	522	0.2%	5.3%	2.7%	91.7%	190	0.3%	0.5%	0.5%	0.0%	98.7%
S	6518	2.8%	0.2%	0.1%	1.3%	0.0%	95.6%	3502	0.0%	87.5%	2.9%	9.6%	1277	0.0%	0.0%	0.1%	5.0%	94.9%
Co	2810	1.8%	1.5%	0.1%	96.7%	0.0%	0.0%	1510	16.3%	0.9%	83.1%	0.2%	550	18.2%	0.9%	2.7%	51.5%	26.8%

KWh/t refined Ni	1388
Electricity	100%
Oil/Gas	0%
Coal	0%
Air	0%

KWh/t refined Ni	927
Electricity	100%
Oil/Gas	0%
Coal	0%
Air	0%

KWh/t refined Ni	927
Electricity	100%
Oil/Gas	0%
Coal	0%
Air	0%

Figure B.32: Data refers to recovery % in Nickel-copper alloy processing in Figure B.29



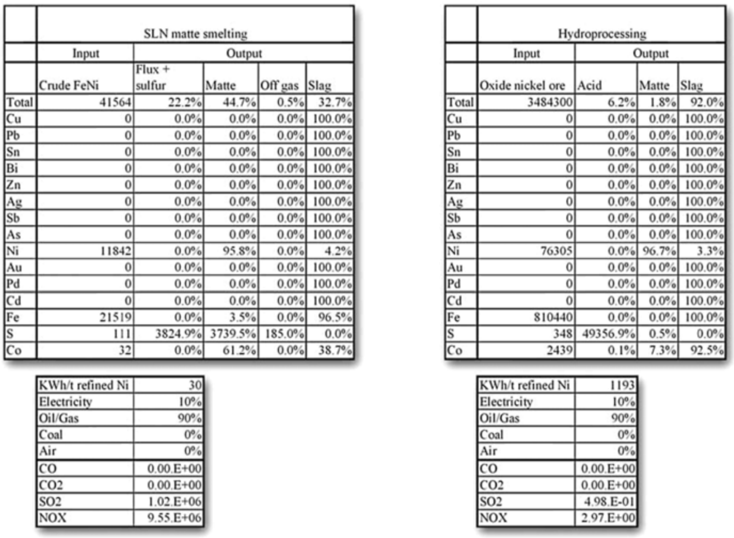
	Hydrochloric acid leach					
	Input	Output				
	Converter matte	Ni	Cu	Co	PGM	Residue
Total	53271	49.8%	28.4%	0.4%	0.1%	21.3%
Cu	13575	0.0%	88.3%	0.0%	0.1%	11.6%
Pb	0	2.9%	92.2%	0.2%	0.0%	4.7%
Sn	0	0.0%	0.0%	0.0%	0.0%	100.0%
Bi	0	0.0%	0.0%	0.0%	0.0%	100.0%
Zn	0	0.0%	0.0%	0.0%	0.0%	100.0%
Ag	0	0.0%	0.0%	0.0%	0.0%	100.0%
Sb	0	0.0%	0.0%	0.0%	0.0%	100.0%
As	0	12.5%	87.6%	0.2%	0.0%	0.0%
Ni	31323	93.8%	0.3%	0.0%	0.0%	5.9%
Au	0	0.0%	0.0%	0.0%	0.0%	100.0%
Pd	0	0.0%	0.0%	0.0%	0.0%	100.0%
Cd	0	0.0%	0.0%	0.0%	0.0%	100.0%
Fe	629	0.2%	0.4%	0.0%	0.9%	98.5%
S	7473	0.0%	0.0%	0.0%	0.1%	99.8%
Co	879	12.2%	0.6%	50.0%	0.1%	37.1%

KWh/t refined Ni	927
Electricity	100%
Oil/Gas	0%
Coal	0%
Air	0%

	Copper elektrolyte treatment			
	Input	Output		
	Copper elektrolyte residue	Ni	Cu	Residue
Total	31323	63.0%	37.0%	0.0%
Cu	30	0.1%	99.9%	0.0%
Pb	0	32.9%	67.1%	0.0%
Sn	0	0.0%	0.0%	100.0%
Bi	0	0.0%	0.0%	100.0%
Zn	0	0.0%	0.0%	100.0%
Ag	0	0.0%	0.0%	100.0%
Sb	0	0.0%	0.0%	100.0%
As	0	3.2%	96.8%	0.0%
Ni	31322	100.0%	0.0%	0.0%
Au	0	0.0%	0.0%	100.0%
Pd	0	0.0%	0.0%	100.0%
Cd	0	0.0%	0.0%	100.0%
Fe	0	0.0%	100.0%	0.0%
S	0	0.0%	100.0%	0.0%
Co	0	15.3%	84.7%	0.0%

KWh/t refined Ni	927
Electricity	100%
Oil/Gas	0%
Coal	0%
Air	0%

Figure B.33: Data refers to recovery % in chloride leach and copper electrolyte processing in Figure B.29



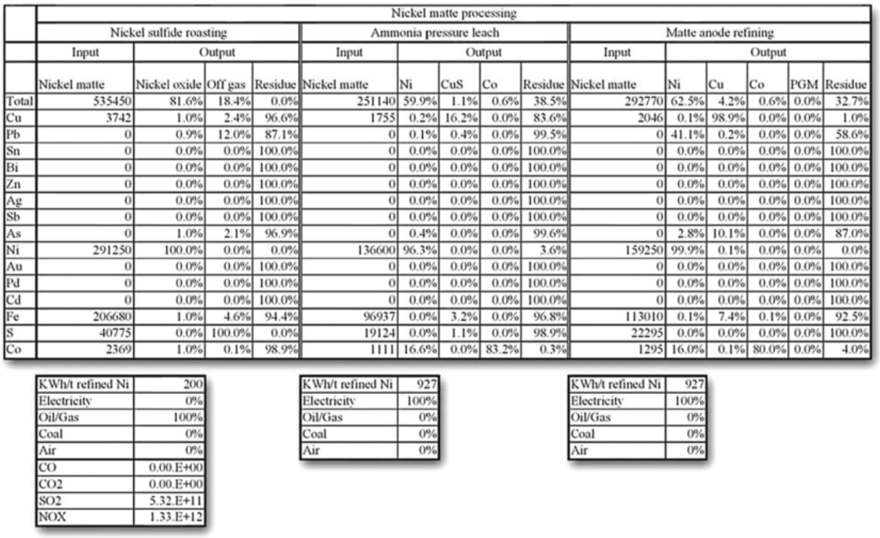
	SLN matte smelting				
	Input	Output			
	Crude FeNi	Flux + sulfur	Matte	Off gas	Slag
Total	41564	22.2%	44.7%	0.5%	32.7%
Cu	0	0.0%	0.0%	0.0%	100.0%
Pb	0	0.0%	0.0%	0.0%	100.0%
Sn	0	0.0%	0.0%	0.0%	100.0%
Bi	0	0.0%	0.0%	0.0%	100.0%
Zn	0	0.0%	0.0%	0.0%	100.0%
Ag	0	0.0%	0.0%	0.0%	100.0%
Sb	0	0.0%	0.0%	0.0%	100.0%
As	0	0.0%	0.0%	0.0%	100.0%
Ni	11842	0.0%	95.8%	0.0%	4.2%
Au	0	0.0%	0.0%	0.0%	100.0%
Pd	0	0.0%	0.0%	0.0%	100.0%
Cd	0	0.0%	0.0%	0.0%	100.0%
Fe	21519	0.0%	3.5%	0.0%	96.5%
S	111	3824.9%	3739.5%	185.0%	0.0%
Co	32	0.0%	61.2%	0.0%	38.7%

KWh/t refined Ni	30
Electricity	10%
Oil/Gas	90%
Coal	0%
Air	0%
CO	0.00.E+00
CO2	0.00.E+00
SO2	1.02.E+06
NOX	9.55.E+06

	Hydroprocessing			
	Input	Output		
	Oxide nickel ore	Acid	Matte	Slag
Total	3484300	6.2%	1.8%	92.0%
Cu	0	0.0%	0.0%	100.0%
Pb	0	0.0%	0.0%	100.0%
Sn	0	0.0%	0.0%	100.0%
Bi	0	0.0%	0.0%	100.0%
Zn	0	0.0%	0.0%	100.0%
Ag	0	0.0%	0.0%	100.0%
Sb	0	0.0%	0.0%	100.0%
As	0	0.0%	0.0%	100.0%
Ni	76305	0.0%	96.7%	3.3%
Au	0	0.0%	0.0%	100.0%
Pd	0	0.0%	0.0%	100.0%
Cd	0	0.0%	0.0%	100.0%
Fe	810440	0.0%	0.0%	100.0%
S	348	49356.9%	0.5%	0.0%
Co	2439	0.1%	7.3%	92.5%

KWh/t refined Ni	1193
Electricity	10%
Oil/Gas	90%
Coal	0%
Air	0%
CO	0.00.E+00
CO2	0.00.E+00
SO2	4.98.E-01
NOX	2.97.E+00

Figure B.34: Data refers to recovery % in SLN Matte smelting and hydroprocessing in Figure B.29



	Nickel matte processing														
	Nickel sulfide roasting				Ammonia pressure leach					Matte anode refining					
	Input	Output			Input	Output				Input	Output				
	Nickel matte	Nickel oxide	Off gas	Residue	Nickel matte	Ni	CuS	Co	Residue	Nickel matte	Ni	Cu	Co	PGM	Residue
Total	535450	81.6%	18.4%	0.0%	251140	59.9%	1.1%	0.6%	38.5%	292770	62.5%	4.2%	0.6%	0.0%	32.7%
Cu	3742	1.0%	2.4%	96.6%	1755	0.2%	16.2%	0.0%	83.6%	2046	0.1%	98.9%	0.0%	0.0%	1.0%
Pb	0	0.9%	12.0%	87.1%	0	0.1%	0.4%	0.0%	99.5%	0	41.1%	0.2%	0.0%	0.0%	58.6%
Sn	0	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%
Bi	0	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%
Zn	0	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%
Ag	0	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%
Sb	0	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%
As	0	1.0%	2.1%	96.9%	0	0.4%	0.0%	0.0%	99.6%	0	2.8%	10.1%	0.0%	0.0%	87.0%
Ni	291250	100.0%	0.0%	0.0%	136600	96.3%	0.0%	0.0%	3.6%	159250	99.9%	0.1%	0.0%	0.0%	0.0%
Au	0	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%
Pd	0	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%
Cd	0	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%
Fe	206680	1.0%	4.6%	94.4%	96937	0.0%	3.2%	0.0%	96.8%	113010	0.1%	7.4%	0.1%	0.0%	92.5%
S	40775	0.0%	100.0%	0.0%	19124	0.0%	1.1%	0.0%	98.9%	22295	0.0%	0.0%	0.0%	0.0%	100.0%
Co	2369	1.0%	0.1%	98.9%	1111	16.6%	0.0%	83.2%	0.3%	1295	16.0%	0.1%	80.0%	0.0%	4.0%

KWh/t refined Ni	200
Electricity	0%
Oil/Gas	100%
Coal	0%
Air	0%
CO	0.00.E+00
CO2	0.00.E+00
SO2	5.32.E+11
NOX	1.33.E+12

KWh/t refined Ni	927
Electricity	100%
Oil/Gas	0%
Coal	0%
Air	0%

KWh/t refined Ni	927
Electricity	100%
Oil/Gas	0%
Coal	0%
Air	0%

Figure B.35: Data refers to recovery % in nickel matte processing in Figure B.29

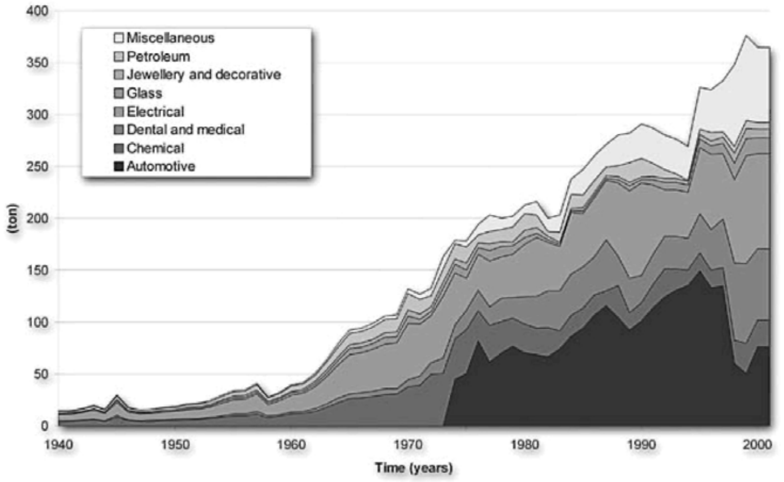


Figure B.36: PGM production and estimated end uses from 1940-2000 [227].

B.6 Platinum Group Metals

Platinum groups metals (PGMs), viz. platinum, palladium, rhodium, iridium, osmium, ruthenium, are produced as by-products from production of other metals.

B.6.1 End uses

In 2000 approximately 19 tons of rhodium, 182 tons of platinum and 227 tons of palladium (Johnson Matthey 2001) were produced. Figure B.36 shows production and the end-uses of the PGMs as a function of time.

B.6.2 Production

The main sources for primary PGMs are ores that are associated with nickel-copper sulphides. As such, these ores are first processed to extract the nickel and copper also producing a PGM rich intermediate. PGMs are also produced from gold by-products. PGMs are circulated between different metal production circuits before the recovery is feasible. The PGM rich concentrates are separated and refined with a variety of complex hydrometallurgical processes sometimes combined with gold production. PGM refining is complex and individual process stages may have to be repeated to achieve the required purity. The number and order of the stages also depends on the contaminants to be removed and the specific mix of PGMs to be separated from any one batch of feedstock. The exact process combinations employed depends on the raw materials mix processed in the refinery. Being of high value, all process routes have high internal recycling rates, and yield recoveries of almost 100%. PGMs are generally recycled at high rates (e.g. car catalysts if they are dismantled from cars). Secondary PGMs can be very concentrated and directly refined to pure PGMs, or are part of complex materials and are processed in different base metal smelters routes and typically concentrated in gold or nickel production to PGM rich residues or precipitates.

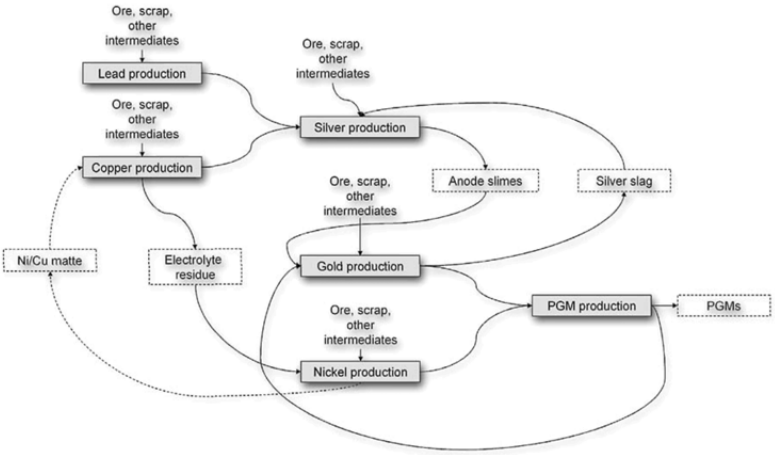


Figure B.37: Simplified PGM production flowchart

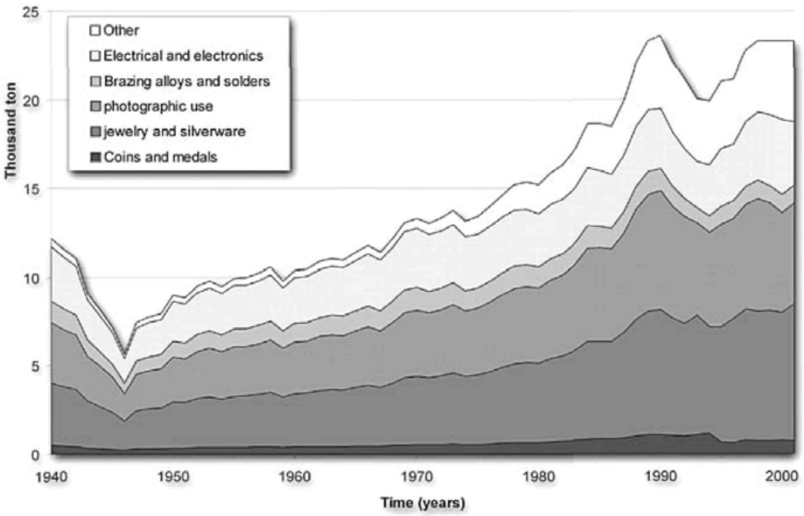


Figure B.38: Silver production and estimated end uses from 1940-2000 [227, 229]

B.7 Silver

B.7.1 End uses

In 2000, approximately 23 thousand tons of silver were produced globally. Silver is produced from lead-zinc ores (38%), copper ores (23%), gold ores (15%) and silver ores (24%) [229]. Silver has been known since ancient times; there is evidence that mankind separated silver from lead as early as 3000 BC [464]. For centuries, silver has traditionally been used for coinage. Only in the last century, it has been replaced by other metals in most countries because of its increased price and industrial usage. Silver is still used for coinage and other traditional applications (jewellry, silverware etc), but is mainly used for its chemical and electronic properties. Particularly, the use of silver for brazing alloys, solders, electrical equipment and electronics has decreased. The ban on lead in electronics in Europe, however, may (partially) reverse this trend as silver is one the potential substitutes for lead in solders. The use of silver for other applications has remained more or less constant. The use of silver for photographic uses may be expected to decrease in the future, as digital photography gains more and more ground.

B.7.2 Production

Each ore or intermediate has its own process to produce crude silver. Silver ores can be treated in several ways. The common practice is to leach the ore in a Pachuca tank with sodium cyanide (co-dissolved from gold ores). The solids are filtered out the solution and the silver is precipitated by cementation with zinc dust. Another process involves the adsorption of the silver cyanide complex on active carbon together with gold cyanide, similar to the carbon-in-pulp process for gold. The silver present in lead-zinc ores follows lead, and is recovered in the refining of lead. Silver is either recovered as Parkes crust in the pyrometallurgical refining, or as anode slimes in the electrolytical refining (see Section B.4). The Parkes crust is processed in the Cupellation process. In the Cupellation process, the smelt is blown with air in order to oxidise the lead, while silver and other precious metals do not react. The lead oxide, litharge, is continuously removed. The produced crude silver is further refined. Anode slimes from copper (Section B.2) and lead electrolysis can contain large amounts of silver and other precious metals. The anode slimes are typically treated in the Doré process. In the Doré furnace fluxes, sodium carbonate, lime, cullet and sand are added to the anode slimes. During melting, these fluxes form a silicate slag that takes up iron, arsenic, antimony, lead, nickel and tin. If the starting materials have a high selenium and tellurium content, also a selenium phase will form between the slag and the matte.

Silver is produced from approximately 30% from secondary materials. These secondary materials come from jewellry, photo materials and from industrial applications and other sources. These materials are treated to extract their silver content. Many routes for silver recovery exist: Photographic film, papers and sludges are incinerated. The ash is recovered and treated with other silver bearing material, the gases are filtered and the dust that is collected is also treated to recover silver. A chemical stripping process in which the silver salts are leached from the emulsion layer is also used. Silver is recovered from waste solutions from the photographic and other industries by chemical precipitation as sulphide to form a powder, which is dried, melted and refined. Alternatively, silver thiosulphate solutions are electrolyzed to produce silver sulphide, which is insoluble and can be recovered. Jewellry can often be recovered by direct remelting. The silver in electronic appliances is typically recovered for the copper value, and return as anode slimes.

B.7.3 Reconciled mass balances

These data represent the distribution of elements between the indicated phases of the unit operations relevant for processing as depicted by Figure B.39. These have been obtained by closing the mass balances by the use of data reconciliation techniques.

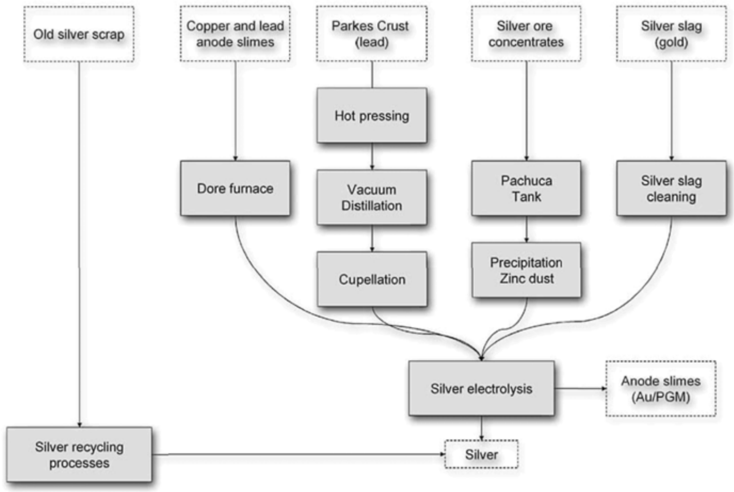
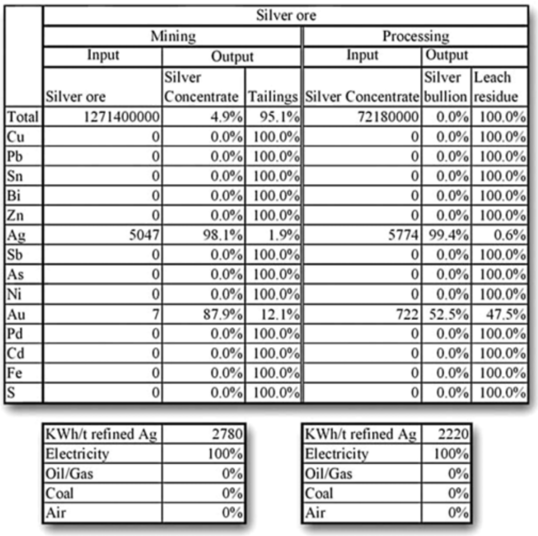


Figure B.39: Simplified silver production flowchart

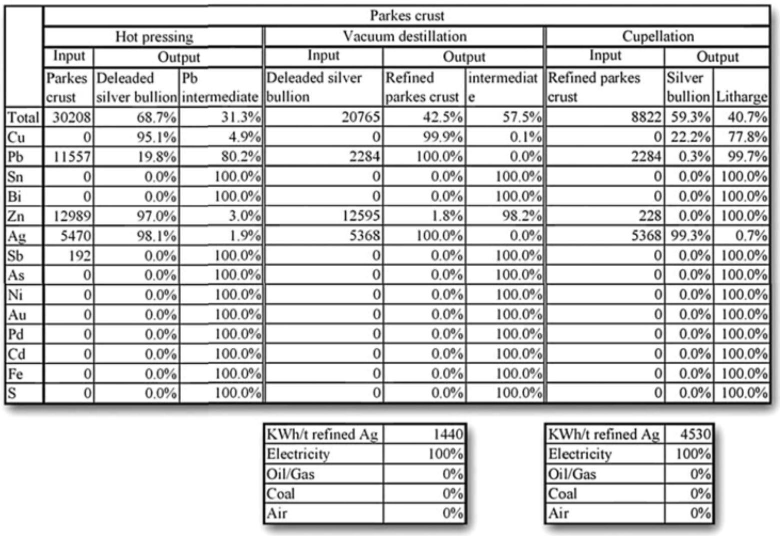


	Silver ore					
	Mining			Processing		
	Input	Output		Input	Output	
	Silver ore	Silver Concentrate	Tailings	Silver Concentrate	Silver bullion	Leach residue
Total	1271400000	4.9%	95.1%	72180000	0.0%	100.0%
Cu	0	0.0%	100.0%	0	0.0%	100.0%
Pb	0	0.0%	100.0%	0	0.0%	100.0%
Sn	0	0.0%	100.0%	0	0.0%	100.0%
Bi	0	0.0%	100.0%	0	0.0%	100.0%
Zn	0	0.0%	100.0%	0	0.0%	100.0%
Ag	5047	98.1%	1.9%	5774	99.4%	0.6%
Sb	0	0.0%	100.0%	0	0.0%	100.0%
As	0	0.0%	100.0%	0	0.0%	100.0%
Ni	0	0.0%	100.0%	0	0.0%	100.0%
Au	7	87.9%	12.1%	722	52.5%	47.5%
Pd	0	0.0%	100.0%	0	0.0%	100.0%
Cd	0	0.0%	100.0%	0	0.0%	100.0%
Fe	0	0.0%	100.0%	0	0.0%	100.0%
S	0	0.0%	100.0%	0	0.0%	100.0%

KWh/t refined Ag	2780
Electricity	100%
Oil/Gas	0%
Coal	0%
Air	0%

KWh/t refined Ag	2220
Electricity	100%
Oil/Gas	0%
Coal	0%
Air	0%

Figure B.40: Data refers to recovery % in Mining and Processing in Figure B.39

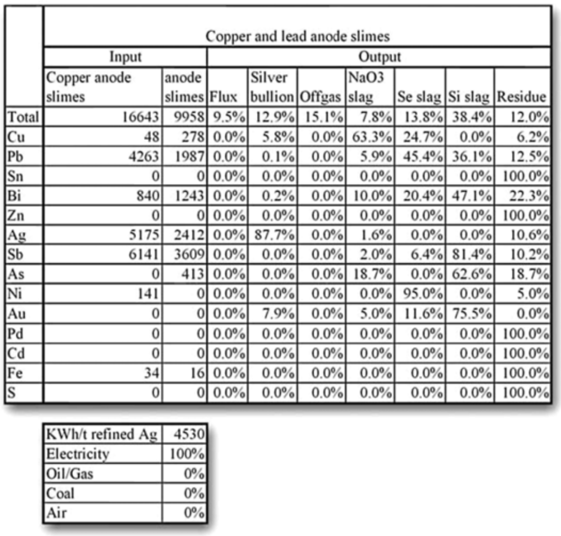


	Parkes crust								
	Hot pressing			Vacuum destillation			Cupellation		
	Input	Output		Input	Output		Input	Output	
	Parkes crust	Deleaded silver bullion	Pb intermediate	Deleaded silver bullion	Refined parkes crust	intermediate	Refined parkes crust	Silver bullion	Litharge
Total	30208	68.7%	31.3%	20765	42.5%	57.5%	8822	59.3%	40.7%
Cu	0	95.1%	4.9%	0	99.9%	0.1%	0	22.2%	77.8%
Pb	11557	19.8%	80.2%	2284	100.0%	0.0%	2284	0.3%	99.7%
Sn	0	0.0%	100.0%	0	0.0%	100.0%	0	0.0%	100.0%
Bi	0	0.0%	100.0%	0	0.0%	100.0%	0	0.0%	100.0%
Zn	12989	97.0%	3.0%	12595	1.8%	98.2%	228	0.0%	100.0%
Ag	5470	98.1%	1.9%	5368	100.0%	0.0%	5368	99.3%	0.7%
Sb	192	0.0%	100.0%	0	0.0%	100.0%	0	0.0%	100.0%
As	0	0.0%	100.0%	0	0.0%	100.0%	0	0.0%	100.0%
Ni	0	0.0%	100.0%	0	0.0%	100.0%	0	0.0%	100.0%
Au	0	0.0%	100.0%	0	0.0%	100.0%	0	0.0%	100.0%
Pd	0	0.0%	100.0%	0	0.0%	100.0%	0	0.0%	100.0%
Cd	0	0.0%	100.0%	0	0.0%	100.0%	0	0.0%	100.0%
Fe	0	0.0%	100.0%	0	0.0%	100.0%	0	0.0%	100.0%
S	0	0.0%	100.0%	0	0.0%	100.0%	0	0.0%	100.0%

KWh/t refined Ag	1440
Electricity	100%
Oil/Gas	0%
Coal	0%
Air	0%

KWh/t refined Ag	4530
Electricity	100%
Oil/Gas	0%
Coal	0%
Air	0%

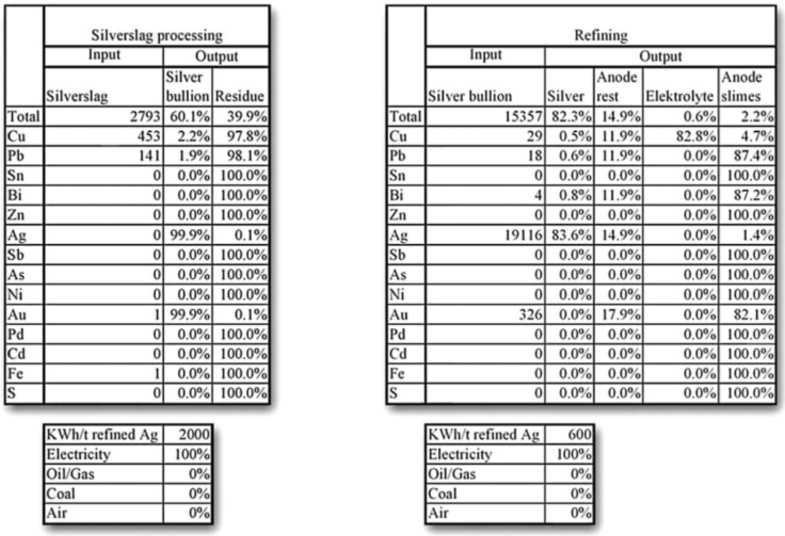
Figure B.41: Data refers to recovery % in processing of Parkes crust in Figure B.39



	Copper and lead anode slimes								
	Input		Output						
	Copper anode slimes	anode slimes	Flux	Silver bullion	Offgas	NaO3 slag	Se slag	Si slag	Residue
Total	16643	9958	9.5%	12.9%	15.1%	7.8%	13.8%	38.4%	12.0%
Cu	48	278	0.0%	5.8%	0.0%	63.3%	24.7%	0.0%	6.2%
Pb	4263	1987	0.0%	0.1%	0.0%	5.9%	45.4%	36.1%	12.5%
Sn	0	0	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	100.0%
Bi	840	1243	0.0%	0.2%	0.0%	10.0%	20.4%	47.1%	22.3%
Zn	0	0	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	100.0%
Ag	5175	2412	0.0%	87.7%	0.0%	1.6%	0.0%	0.0%	10.6%
Sb	6141	3609	0.0%	0.0%	0.0%	2.0%	6.4%	81.4%	10.2%
As	0	413	0.0%	0.0%	0.0%	18.7%	0.0%	62.6%	18.7%
Ni	141	0	0.0%	0.0%	0.0%	0.0%	95.0%	0.0%	5.0%
Au	0	0	0.0%	7.9%	0.0%	5.0%	11.6%	75.5%	0.0%
Pd	0	0	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	100.0%
Cd	0	0	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	100.0%
Fe	34	16	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	100.0%
S	0	0	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	100.0%

KWh/t refined Ag	4530
Electricity	100%
Oil/Gas	0%
Coal	0%
Air	0%

Figure B.42: Data refers to recovery % in copper and lead anodes slimes processing in Figure B.39



	Silverslag processing		
	Input	Output	
	Silverslag	Silver bullion	Residue
Total	2793	60.1%	39.9%
Cu	453	2.2%	97.8%
Pb	141	1.9%	98.1%
Sn	0	0.0%	100.0%
Bi	0	0.0%	100.0%
Zn	0	0.0%	100.0%
Ag	0	99.9%	0.1%
Sb	0	0.0%	100.0%
As	0	0.0%	100.0%
Ni	0	0.0%	100.0%
Au	1	99.9%	0.1%
Pd	0	0.0%	100.0%
Cd	0	0.0%	100.0%
Fe	1	0.0%	100.0%
S	0	0.0%	100.0%

KWh/t refined Ag	2000
Electricity	100%
Oil/Gas	0%
Coal	0%
Air	0%

	Refining				
	Input	Output			
	Silver bullion	Silver	Anode rest	Elektrolyte	Anode slimes
Total	15357	82.3%	14.9%	0.6%	2.2%
Cu	29	0.5%	11.9%	82.8%	4.7%
Pb	18	0.6%	11.9%	0.0%	87.4%
Sn	0	0.0%	0.0%	0.0%	100.0%
Bi	4	0.8%	11.9%	0.0%	87.2%
Zn	0	0.0%	0.0%	0.0%	100.0%
Ag	19116	83.6%	14.9%	0.0%	1.4%
Sb	0	0.0%	0.0%	0.0%	100.0%
As	0	0.0%	0.0%	0.0%	100.0%
Ni	0	0.0%	0.0%	0.0%	100.0%
Au	326	0.0%	17.9%	0.0%	82.1%
Pd	0	0.0%	0.0%	0.0%	100.0%
Cd	0	0.0%	0.0%	0.0%	100.0%
Fe	0	0.0%	0.0%	0.0%	100.0%
S	0	0.0%	0.0%	0.0%	100.0%

KWh/t refined Ag	600
Electricity	100%
Oil/Gas	0%
Coal	0%
Air	0%

Figure B.43: Data refers to recovery % in silver slag and bullion refining in Figure B.39

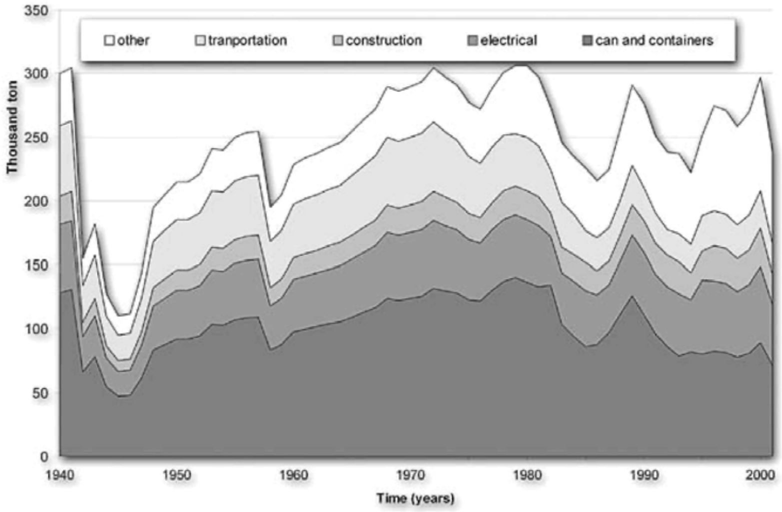


Figure B.44: Tin production and estimated end uses from 1940-2000 [227, 464]

B.8 Tin production and recycling profile

B.8.1 End uses

In 2000 about 297 thousand tons were produced globally. Unlike the other metals, the global production of tin remained more or less constant from 1940 to 2000. Tin has been known to mankind since at least 3500 BC [464]. Tin has the lowest melting point (232°C) of the common metals, is corrosion resistant, and readily forms a wide range of useful alloys. Cans and containers are its main end use. It is also used for the production of electrical appliances, construction, transportation and a large number of other, smaller end uses. These include paints, toothpaste, plastics, tin chemicals, tin foil, collapsible tubes, organ pipes, liners for valves and pipes, molten baths for float glass, and tin powder for lowering the sintering temperature of powder metallurgy pads. Figure B.44 shows the trends in the end uses of tin from 1972 to 2002. The use of tin for cans and containers is slowly decreasing, due to a falling proportion of tin in tinplated steel, and the rise of substitutes for tinplated steel such as aluminium, plastics and tin-free steel (e.g. coated with a thin film of chromium/chromium oxide). In addition, the combination of a thin film of plastic and tin reduces the use of tin. Particularly, food and drink cans are increasingly made of aluminium, or other substitutes. The substitution of lead in electronics and electrical equipment (in the EU) may lead to an increased use of tin for electronics, as many lead-free solders contain higher amounts of tin than the conventional lead-tin solders.

B.8.2 Production

Tin is mainly produced from sulphide (25%) and oxide ores (75%), a small fraction is produced from the intermediates of the production of other metals (e.g. from secondary copper production). A head grade for both ores of 0.7-2% is common, usually concentrated to 40-70% prior to shipment for metal production [470, 474]. Sulphide ores are first roasted to an oxidic concentrate. In the roasting process, the tin sulphides are oxidized, and major oxidic impurities, such as arsenic, are volatized. Roasting is usually carried out in rotary kilns. The roast product and the concentrated oxidic ore are reduced in two steps to crude tin. The first stage gives a relative pure metal and a tin rich slag. This slag is treated in a second stage to extract the tin. Various kinds of furnaces are used for treating tin concentrates, each with its advantages and disadvantages. The most commonly used furnaces are the reverberatory furnace (48%), the rotary air furnace (26%), the electric furnace (8%), and the Ausmelt furnace (18%). A reverberatory furnace is a rectangular furnace with burners located at the narrow sides of the furnace. The furnace, operated in batches, is charged with concentrate, carbon and flux. The carbon reduces the tin oxide to tin. The partial pressure of carbon monoxide in the furnace determines the efficiency of the furnace. Rotary kiln furnaces are horizontal smelting units that also operate batch wise, and are based on the same metallurgy. In comparison to reverberatory furnaces, they have larger melting capacities, but also higher stress on the refractory lining and higher energy requirements. Electric furnaces are circular furnaces that reduce the tin oxide to tin by electrical current. The three-phase electric arc currents through carbon electrodes reduce the tin oxides and provide for the process heat. When the concentrate has low levels of iron, the electric furnace can produce a crude tin in a single stage. The Ausmelt is a cylindrical furnace in which a vertical lance is mounted. The furnace is heated by submerging the lance in the bath, and feeding fuel and air through the lance. This also provides for rigorous mixing and thus good interaction between the different phases in the melt. The slag produced in the tin smelting contains 10-20% tin. The tin in the slag is recovered either by employing a strongly reducing smelt process producing a tin-iron alloy, hardhead, which is recycled to the tin smelting process, or by a blowing process, in which the tin is oxidized to a flue dust that is also recycled back to the tin smelting.

Tin is the most difficult of the common metals to refine. For many years pure tin has only been available from very pure ores, and refining has been practiced only by countries with impure ores and secondary smelters [475]. The crude tin is purified by pyrometallurgical methods (an estimated 40%) or through electrorefining (an estimated 60%). In pyrometallurgical refining iron, copper, arsenic, lead and bismuth are stepwise removed: (i) iron is removed by liquation and the precipitated iron is separated from the tin by passing steam, or air through the melt, (ii) copper is removed by reaction with elemental sulphur and skimming off the resulting copper dross, (iii) arsenic is removed, together with some nickel, copper and iron, by formation of intermetallic compounds with aluminum, (iv) lead is removed by treatment with chlorine, which will convert it into lead dichloride, (v) in the last step bismuth is removed by precipitation with calcium or magnesium. Electrorefining of tin is only employed when the crude tin contains high concentrations of noble metals: The process can only be operated at low current densities, and has a relatively low efficiency. As electrolyte both an acid, sulphate electrolyte, or an alkaline, sodium hydroxide (NaOH) electrolyte, medium can be used. Approximately 27% of the global tin production is produced from secondary materials. New scrap accounts for 11%, and old scrap for 16%. Tin is used as a coating on other metals, alloying metal with one or more other metals. Tin containing products (old scrap) are typically recycled for their content of other metals. The major end use and source of secondary tin is tin-plated steel. In the recycling, the steel is treated electrolytically to remove the tin in de-tinning facilities. Similarly, tin in electronics (e.g. solders) is typically recycled in copper processes.

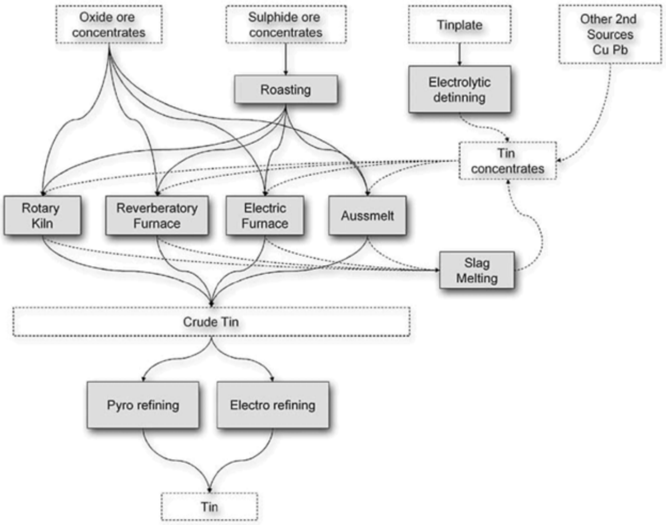
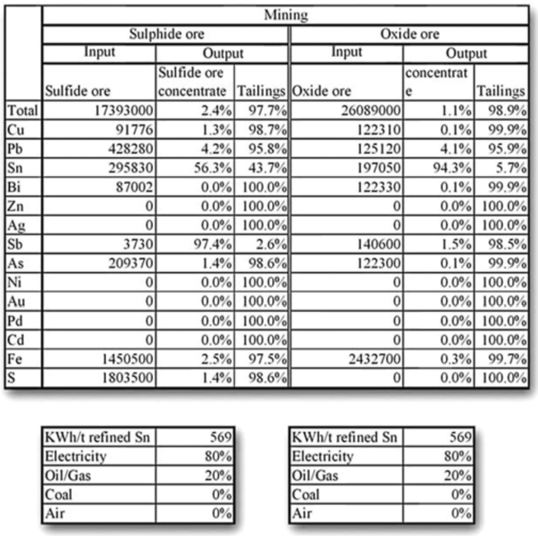


Figure B.45: Simplified tin production flowchart

B.8.3 Reconciled mass balances

These data represent the distribution of elements between the indicated phases of the unit operations relevant for processing as depicted by Figure B.45. These have been obtained by closing the mass balances by the use of data reconciliation techniques.



	Mining					
	Sulphide ore			Oxide ore		
	Input	Output		Input	Output	
	Sulfide ore	Sulfide ore concentrate	Tailings	Oxide ore	concentrate	Tailings
Total	17393000	2.4%	97.7%	26089000	1.1%	98.9%
Cu	91776	1.3%	98.7%	122310	0.1%	99.9%
Pb	428280	4.2%	95.8%	125120	4.1%	95.9%
Sn	295830	56.3%	43.7%	197050	94.3%	5.7%
Bi	87002	0.0%	100.0%	122330	0.1%	99.9%
Zn	0	0.0%	100.0%	0	0.0%	100.0%
Ag	0	0.0%	100.0%	0	0.0%	100.0%
Sb	3730	97.4%	2.6%	140600	1.5%	98.5%
As	209370	1.4%	98.6%	122300	0.1%	99.9%
Ni	0	0.0%	100.0%	0	0.0%	100.0%
Au	0	0.0%	100.0%	0	0.0%	100.0%
Pd	0	0.0%	100.0%	0	0.0%	100.0%
Cd	0	0.0%	100.0%	0	0.0%	100.0%
Fe	1450500	2.5%	97.5%	2432700	0.3%	99.7%
S	1803500	1.4%	98.6%	0	0.0%	100.0%

KWh/t refined Sn	569
Electricity	80%
Oil/Gas	20%
Coal	0%
Air	0%

KWh/t refined Sn	569
Electricity	80%
Oil/Gas	20%
Coal	0%
Air	0%

Figure B.46: Data refers to recovery % in Mining in Figure B.45

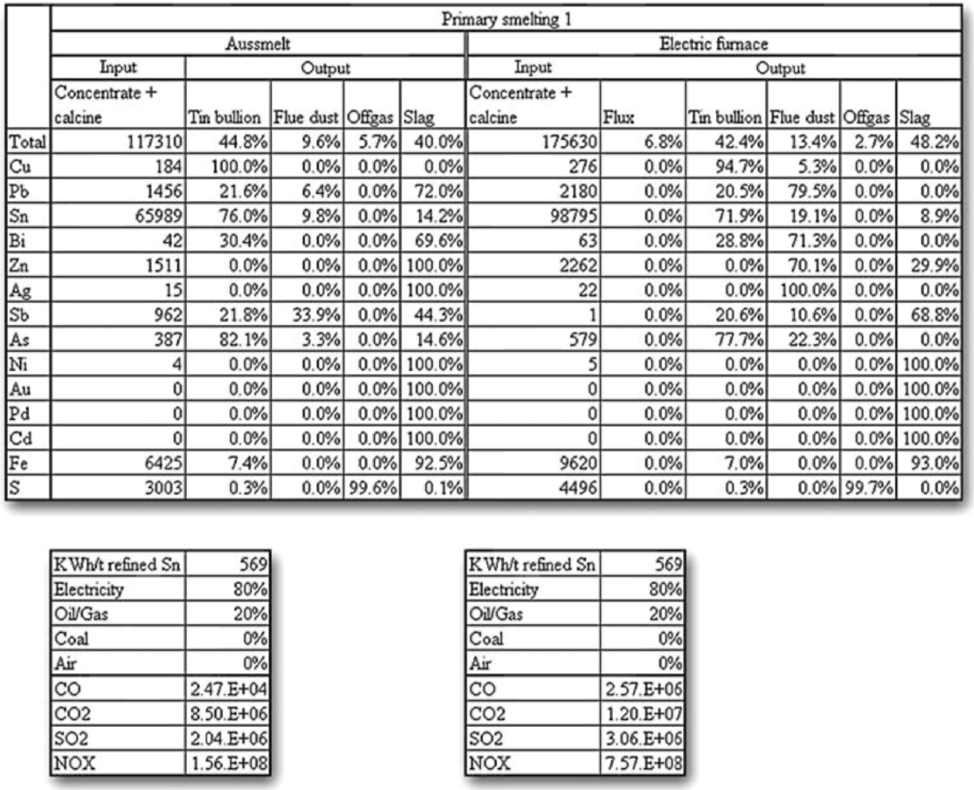
	Roasting			
	Input	Output		
	Sulfide ore concentrate	Calcine	Offgas	Fume
Total	406710	94.6%	5.1%	0.3%
Cu	1195	99.9%	0.0%	0.1%
Pb	1778	93.1%	0.0%	6.9%
Sn	165840	100.0%	0.0%	0.0%
Bi	1	90.4%	26.7%	17.1%
Zn	8338	0.0%	0.0%	100.0%
Ag	102	0.0%	0.0%	100.0%
Sb	3619	98.0%	0.0%	2.0%
As	2987	96.6%	0.0%	3.4%
Ni	0	0.0%	0.0%	100.0%
Au	0	0.0%	0.0%	100.0%
Pd	0	0.0%	0.0%	100.0%
Cd	0	0.0%	0.0%	100.0%
Fe	36121	99.5%	0.0%	0.5%
S	25694	26.4%	73.4%	0.2%

KWh/t refined Sn	569
Electricity	80%
Oil/Gas	20%
Coal	0%
Air	0%
CO	6.19.E+06
CO2	0.00.E+00
SO2	3.77.E+04
NOX	6.94.E+08

	Slag cleaning			
	Input	Output		
	Slag	Hardhead	Fume	Slag
Total	302320	47.5%	2.5%	50.0%
Cu	2	39.0%	0.0%	61.0%
Pb	38141	98.3%	1.7%	0.0%
Sn	46380	70.3%	5.7%	24.0%
Bi	46	1.8%	96.3%	1.9%
Zn	7060	69.9%	0.0%	30.1%
Ag	67	0.0%	0.0%	100.0%
Sb	11596	98.9%	1.0%	0.1%
As	137	98.6%	0.0%	1.4%
Ni	20	0.0%	0.0%	100.0%
Au	0	0.0%	0.0%	100.0%
Pd	0	0.0%	0.0%	100.0%
Cd	0	0.0%	0.0%	100.0%
Fe	33713	66.9%	0.5%	32.7%
S	14	0.0%	0.0%	100.0%

KWh/t refined Sn	569
Electricity	80%
Oil/Gas	20%
Coal	0%
Air	0%
CO	1.06.E+07
CO2	1.74.E+07
SO2	0.00.E+00
NOX	4.06.E+07

Figure B.47: Data refers to recovery % in Roasting and Slag Cleaning in Figure B.45



	Primary smelting 1										
	Aussmelt					Electric furnace					
	Input	Output				Input	Output				
	Concentrate + calcine	Tin bullion	Flue dust	Offgas	Slag	Concentrate + calcine	Flux	Tin bullion	Flue dust	Offgas	Slag
Total	117310	44.8%	9.6%	5.7%	40.0%	175630	6.8%	42.4%	13.4%	2.7%	48.2%
Cu	184	100.0%	0.0%	0.0%	0.0%	276	0.0%	94.7%	5.3%	0.0%	0.0%
Pb	1456	21.6%	6.4%	0.0%	72.0%	2180	0.0%	20.5%	79.5%	0.0%	0.0%
Sn	65989	76.0%	9.8%	0.0%	14.2%	98795	0.0%	71.9%	19.1%	0.0%	8.9%
Bi	42	30.4%	0.0%	0.0%	69.6%	63	0.0%	28.8%	71.3%	0.0%	0.0%
Zn	1511	0.0%	0.0%	0.0%	100.0%	2262	0.0%	0.0%	70.1%	0.0%	29.9%
Ag	15	0.0%	0.0%	0.0%	100.0%	22	0.0%	0.0%	100.0%	0.0%	0.0%
Sb	962	21.8%	33.9%	0.0%	44.3%	1	0.0%	20.6%	10.6%	0.0%	68.8%
As	387	82.1%	3.3%	0.0%	14.6%	579	0.0%	77.7%	22.3%	0.0%	0.0%
Ni	4	0.0%	0.0%	0.0%	100.0%	5	0.0%	0.0%	0.0%	0.0%	100.0%
Au	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%
Pd	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%
Cd	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%
Fe	6425	7.4%	0.0%	0.0%	92.5%	9620	0.0%	7.0%	0.0%	0.0%	93.0%
S	3003	0.3%	0.0%	99.6%	0.1%	4496	0.0%	0.3%	0.0%	99.7%	0.0%

KWh/t refined Sn	569
Electricity	80%
Oil/Gas	20%
Coal	0%
Air	0%
CO	2.47.E+04
CO2	8.50.E+06
SO2	2.04.E+06
NOX	1.56.E+08

KWh/t refined Sn	569
Electricity	80%
Oil/Gas	20%
Coal	0%
Air	0%
CO	2.57.E+06
CO2	1.20.E+07
SO2	3.06.E+06
NOX	7.57.E+08

Figure B.48: Data refers to recovery % in Ausmelt and Electric furnace smelting in Figure B.45

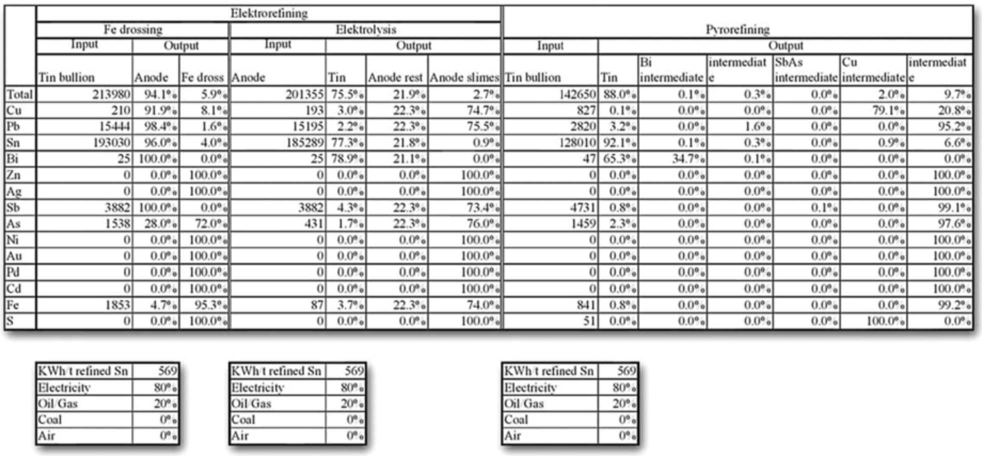
	Secondary smelting															
	Aussmelt					Electric furnace						Reverberatory furnace				
	Input	Output				Input		Output				Input		Output		
	Tin scrap	Tin bullion	Flue dust	Offgas	Slag	Tin scrap	Flux	Tin bullion	Flue dust	Offgas	Slag	Tin scrap	Flux	Tin bullion	Flue dust	Offgas	Slag
Total	26362	44.8%	9.6%	5.7%	40.0%	39474	6.8%	42.4%	13.4%	2.7%	48.2%	72046	2.1%	44.8%	12.7%	17.3%	27.3%
Cu	0	100.0%	0.0%	0.0%	0.0%	0	0.0%	94.7%	5.3%	0.0%	0.0%	0	0.0%	99.9%	0.1%	0.0%	0.0%
Pb	14787	21.6%	6.4%	0.0%	72.0%	22142	0.0%	20.5%	79.5%	0.0%	0.0%	40412	0.0%	21.7%	19.8%	0.0%	58.5%
Sn	9879	76.0%	9.8%	0.0%	14.2%	14792	0.0%	71.9%	19.1%	0.0%	8.9%	26998	0.0%	76.0%	14.9%	0.0%	9.1%
Bi	0	30.4%	0.0%	0.0%	69.6%	0	0.0%	28.8%	71.3%	0.0%	0.0%	0	0.0%	30.4%	68.7%	0.0%	0.9%
Zn	1	0.0%	0.0%	0.0%	100.0%	1	0.0%	0.0%	70.1%	0.0%	29.9%	2	0.0%	0.0%	0.0%	0.0%	100.0%
Ag	1	0.0%	0.0%	0.0%	100.0%	2	0.0%	0.0%	100.0%	0.0%	0.0%	4	0.0%	0.0%	0.0%	0.0%	100.0%
Sb	6615	21.8%	33.9%	0.0%	44.3%	9905	0.0%	20.6%	10.6%	0.0%	68.8%	18078	0.0%	21.8%	77.9%	0.0%	0.3%
As	286	82.1%	3.3%	0.0%	14.6%	428	0.0%	77.7%	22.3%	0.0%	0.0%	780	0.0%	82.1%	17.8%	0.0%	0.1%
Ni	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%
Au	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%
Pd	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%
Cd	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%
Fe	0	7.4%	0.0%	0.0%	92.5%	0	0.0%	7.0%	0.0%	0.0%	93.0%	0	0.0%	7.4%	0.0%	0.0%	92.5%
S	0	0.3%	0.0%	99.6%	0.1%	0	0.0%	0.3%	0.0%	99.7%	0.0%	0	0.0%	0.3%	0.0%	99.6%	0.1%

KWh/t refined Sn	569
Electricity	80%
Oil/Gas	20%
Coal	0%
Air	0%
CO	4.86.E+04
CO2	1.59.E+06
SO2	0.00.E+00
NOX	4.76.E+07

KWh/t refined Sn	569
Electricity	80%
Oil/Gas	20%
Coal	0%
Air	0%
CO	2.01.E+05
CO2	2.26.E+06
SO2	0.00.E+00
NOX	1.90.E+08

KWh/t refined Sn	569
Electricity	80%
Oil/Gas	20%
Coal	0%
Air	0%
CO	1.30.E+05
CO2	4.35.E+06
SO2	0.00.E+00
NOX	3.67.E+08

Figure B.49: Data refers to recovery % in secondary smelting in Figure B.45



	Elektrorefining							Pyrorefining						
	Fe drossing			Elektrolysis										
	Input	Output		Input	Output			Input	Output					
	Tin bullion	Anode	Fe dross	Anode	Tin	Anode rest	Anode slimes	Tin bullion	Tin	Bi intermediate	intermediate	SbAs intermediate	Cu intermediate	intermediate
Total	213980	94.1%	5.9%	201355	75.5%	21.9%	2.7%	142650	88.0%	0.1%	0.3%	0.0%	2.0%	9.7%
Cu	210	91.9%	8.1%	193	3.0%	22.3%	74.7%	827	0.1%	0.0%	0.0%	0.0%	79.1%	20.8%
Pb	15444	98.4%	1.6%	15195	2.2%	22.3%	75.5%	2820	3.2%	0.0%	1.6%	0.0%	0.0%	95.2%
Sn	193030	96.0%	4.0%	185289	77.3%	21.8%	0.9%	128010	92.1%	0.1%	0.3%	0.0%	0.9%	6.6%
Bi	25	100.0%	0.0%	25	78.9%	21.1%	0.0%	47	65.3%	34.7%	0.1%	0.0%	0.0%	0.0%
Zn	0	0.0%	100.0%	0	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	0.0%	100.0%
Ag	0	0.0%	100.0%	0	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	0.0%	100.0%
Sb	3882	100.0%	0.0%	3882	4.3%	22.3%	73.4%	4731	0.8%	0.0%	0.0%	0.1%	0.0%	99.1%
As	1538	28.0%	72.0%	431	1.7%	22.3%	76.0%	1459	2.3%	0.0%	0.0%	0.0%	0.0%	97.6%
Ni	0	0.0%	100.0%	0	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	0.0%	100.0%
Au	0	0.0%	100.0%	0	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	0.0%	100.0%
Pd	0	0.0%	100.0%	0	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	0.0%	100.0%
Cd	0	0.0%	100.0%	0	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	0.0%	100.0%
Fe	1853	4.7%	95.3%	87	3.7%	22.3%	74.0%	841	0.8%	0.0%	0.0%	0.0%	0.0%	99.2%
S	0	0.0%	100.0%	0	0.0%	0.0%	100.0%	51	0.0%	0.0%	0.0%	0.0%	100.0%	0.0%

KWh/t refined Sn	569
Electricity	80%
Oil/Gas	20%
Coal	0%
Air	0%

KWh/t refined Sn	569
Electricity	80%
Oil/Gas	20%
Coal	0%
Air	0%

KWh/t refined Sn	569
Electricity	80%
Oil/Gas	20%
Coal	0%
Air	0%

Figure B.50: Data refers to recovery % in Electro- and pyro-refining in Figure B.45

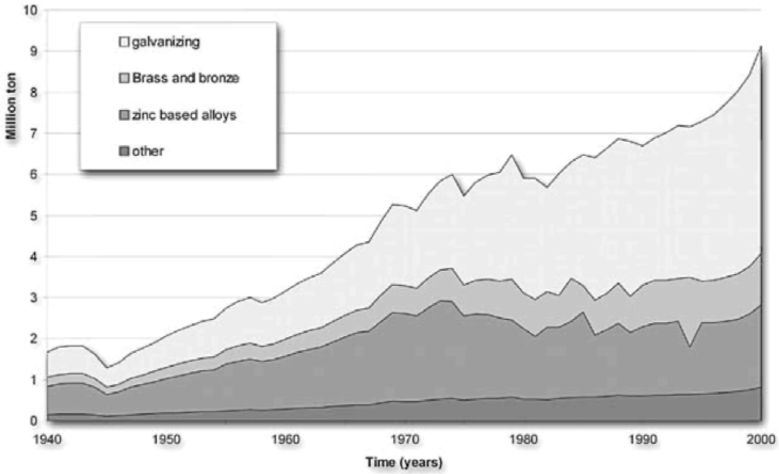


Figure B.51: Zinc production and estimated end uses from 1940-2000 [227, 226]

B.9 Zinc production and recycling profile

B.9.1 End uses

In 2000, 6.65 million tons of zinc was produced. Increasingly, the most important use of zinc is the galvanizing of steel, which consumes approximately half of the zinc produced. About two third of the zinc for galvanizing is used in transport (automobiles, trucks, and ships) and construction (infrastructure, buildings and factories). Other important galvanizing end uses are electrical equipment, air condition and heating. The balance is used for wire, fencing, tanks, pipes and other smaller end uses such as nails and fasteners. Zinc-based alloys (excluding brass and bronze) are the second largest end use. These alloys are mainly used in automobiles and trucks, construction, electrical components and (industrial, agricultural and commercial) machinery and some general appliances. A small amount is used for sporting goods, toys, and scientific equipment and sound and television products. The third largest end use of zinc is brass, and bronze (and some other alloys). About two third is used in electrical and electronic products, industrial machinery, and transportation equipment. The remainder is used in consumer and general products, and in building and construction. The "other" end uses of zinc in Figure B.51 consist of rolled zinc, zinc dust and chemicals. Zinc chemicals are mostly used in rubber production and agriculture. Paints and pigments are also an important application. To a lesser extent, zinc chemicals are also used in ceramics, electronics, photocopying, chemicals (processing), and pharmaceutical and consumer products. The most important application of zinc dust and rolled zinc is coinages, followed by batteries and consumer items. Rolled zinc and zinc dust is also used in metallurgical processes and chemicals production, for printing plates, paints and pigments, the dying of textiles, concrete roofing and gutters.

B.9.2 Production

Zinc is found as sulphide ore, in open pit (8%), underground mines (80%) and combined mining operations (12%). A head grade of zinc ore of 3-9% is common, typically concentrated to about 50%. The majority of the zinc ore (80%) is processed with the hydrometallurgical Roasting-Leach-Electrowinning (RLE) route. The balance is produced via the pyrometallurgical route, the Imperial Smelter process. The pyrometallurgical routes are generally used to process complex ores, or other zinc containing materials (secondary materials), with a high lead content. Zinc-containing residues from lead smelting or other processes, or secondary material with low zinc content are processed in a Waelz kiln or a slag fuming process (Figure B.52) to zinc oxide. The zinc oxide can be sold directly, or further refined in the ISF or hydrometallurgical route. The pyrometallurgical route has higher fuel consumption and emissions than the hydrometallurgical route, but (often) produces a waste product that is environmentally easier to discard.

The hydrometallurgical RLE route can be divided into three steps: (i) roasting, (ii) leaching, (iii) electrolysis. In the roasting step, the concentrate is calcined (oxidized) in a fluid bed roaster. Next, the calcine is leached in a neutral leach: the oxides are dissolved in a dilute sulphuric acid solution. The residue is further leached to recover the remaining zinc and to remove iron as a residue. Depending on the leach processes, different iron-containing residues are produced, viz. jarosite (84%), hematite (12%) or goethite (4%). These residues are a major environmental problem, as a good treatment of these residues has not been found. The zinc recovered in the second leach is fed back to the neutral leach. The zinc solution from the neutral leach is purified using zinc dust. In most cases, the removed metals (copper, cadmium, nickel and cobalt) can be sold as a by-product. The zinc in the purified solution is finally recovered as high purity zinc by electrolysis. The reductive smelting in the Imperial Smelter Furnace produces crude zinc, as well as impure cadmium and lead bullion (Section B.4). The crude zinc is refined by distillation to obtain a high purity product. The crude zinc contains typical impurities such as lead, cadmium and iron, as well as some copper, arsenic and other impurities, depending on the composition of the ore. The distillation process is based on the difference in boiling points of the species: zinc has a relatively low boiling point (906°C) compared to the boiling points of the main impurities, lead (1740°C) and iron (2735°C). Cadmium has a lower boiling than zinc, namely 767°C. The distillation is usually carried out in a system of two columns and a condenser. The molten feed is introduced to the middle of the first column, which is externally heated at the bottom to a temperature of about 1100°C, evaporating zinc and cadmium, which are withdrawn at the top and led to the condenser. The melt, at the bottom, exists mainly of zinc, but with about twice as much lead as in the crude zinc. This can be sold as such, or can be treated to obtain two molten phases, a zinc rich phase (the hard zinc), and a lead rich phase (which can be recycled). Iron and copper also report to the molten phase of the first column. The molten zinc/cadmium mixture from the condenser is fed to the second column with a lower temperature (ca. 950°C), allowing zinc to remain in the condensed state and evaporating cadmium. An impure cadmium canister is obtained at the top of the tower. The final product is high purity zinc. About 31% of the world's zinc supply (nearly 2.9 million tons) comes from recycled zinc, including new scrap (22%). An estimated 80% of the old and new zinc scrap available for recycling is currently recycled [168]. Consumer products containing zinc are mostly treated for their iron content by steel plants (typically electric arc furnaces). Secondary zinc can also be obtained from products treated for their lead or copper content. Brass has a high copper content (>60%) and is recycled almost exclusively by the (brass and) copper industries, which is financially the most attractive route [168]. Some old zinc scrap is obtained directly, such as scrap zinc sheet from

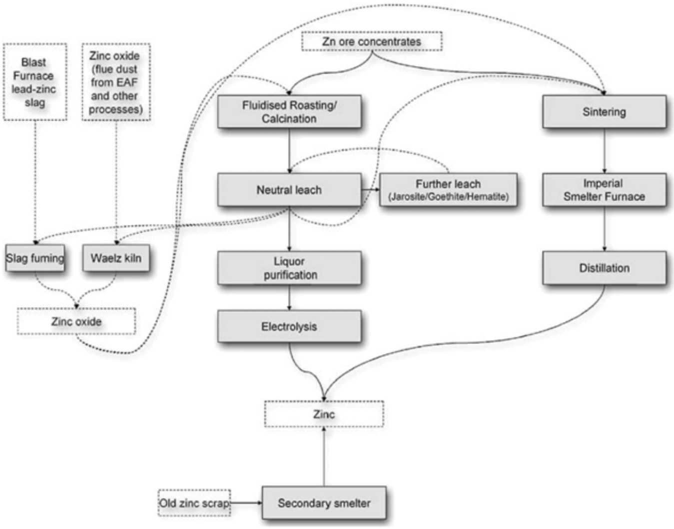
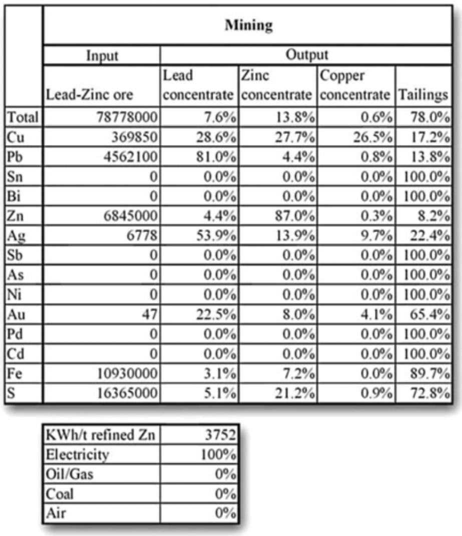


Figure B.52: Simplified zinc production flowchart building applications. As secondary material can contain impurities that would cause severe problems in electrolytic zinc production, they are typically processed in pyrometallurgical processes. The Waelz kiln process is used to enrich and purify (lead and) zinc materials to a product with over 45% of zinc. The raw material for a Waelz kiln can be the slags, flue dusts and sludges arising from zinc production, the slag from lead production, if the zinc content is high enough, the flue dust from the electric arc furnace (EAF). Most of the secondary zinc arises from recycling galvanized steel in an EAF, where the zinc is captured as an oxide in the flue dust. The ISF can also treat flue dusts from EAFs or copper processes (up to 15%). The Waelz kiln is a slightly inclined rotary kiln. In the reactor, zinc oxide is vapourized and reacted with carbon to form zinc vapour. This zinc vapour is collected in the dust bags. The product is an impure grade of zinc oxide containing 50 to 60% zinc that is usually calcined in a rotary kiln to produce clinker oxide. In slag fuming, slag from lead smelting - containing up to 20% zinc oxide - is processed to produce a high-grade zinc oxide. The zinc oxide from these processes can either be sold as a product, or used as a feed to other zinc processes.

B.9.3 Reconciled mass balances

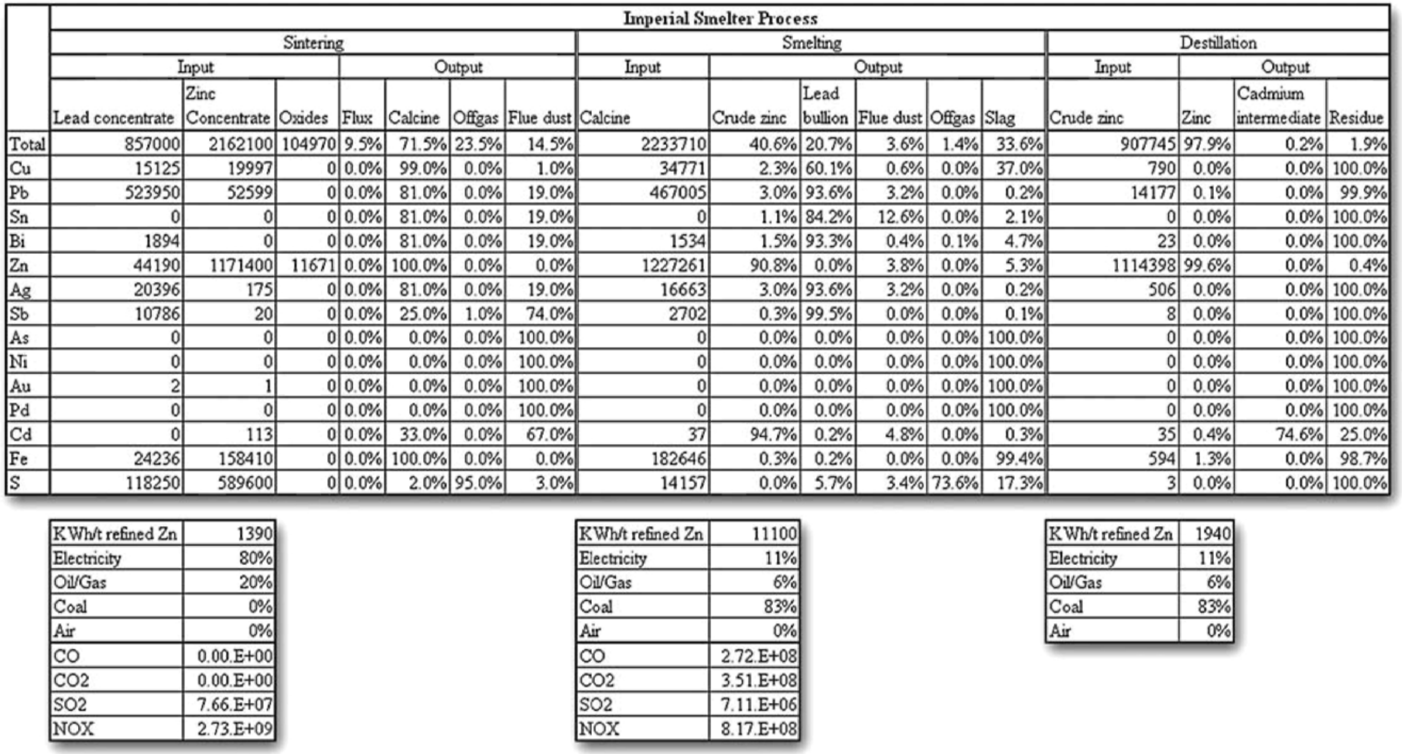
These data represent the distribution of elements between the indicated phases of the unit operations relevant for processing as depicted by Figure B.52. These have been obtained by closing the mass balances by the use of data reconciliation techniques.



	Mining				
	Input	Output			
	Lead-Zinc ore	Lead concentrate	Zinc concentrate	Copper concentrate	Tailings
Total	78778000	7.6%	13.8%	0.6%	78.0%
Cu	369850	28.6%	27.7%	26.5%	17.2%
Pb	4562100	81.0%	4.4%	0.8%	13.8%
Sn	0	0.0%	0.0%	0.0%	100.0%
Bi	0	0.0%	0.0%	0.0%	100.0%
Zn	6845000	4.4%	87.0%	0.3%	8.2%
Ag	6778	53.9%	13.9%	9.7%	22.4%
Sb	0	0.0%	0.0%	0.0%	100.0%
As	0	0.0%	0.0%	0.0%	100.0%
Ni	0	0.0%	0.0%	0.0%	100.0%
Au	47	22.5%	8.0%	4.1%	65.4%
Pd	0	0.0%	0.0%	0.0%	100.0%
Cd	0	0.0%	0.0%	0.0%	100.0%
Fe	10930000	3.1%	7.2%	0.0%	89.7%
S	16365000	5.1%	21.2%	0.9%	72.8%

KWh/t refined Zn	3752
Electricity	100%
Oil/Gas	0%
Coal	0%
Air	0%

Figure B.53: Data refers to recovery % in Mining in Figure B.52



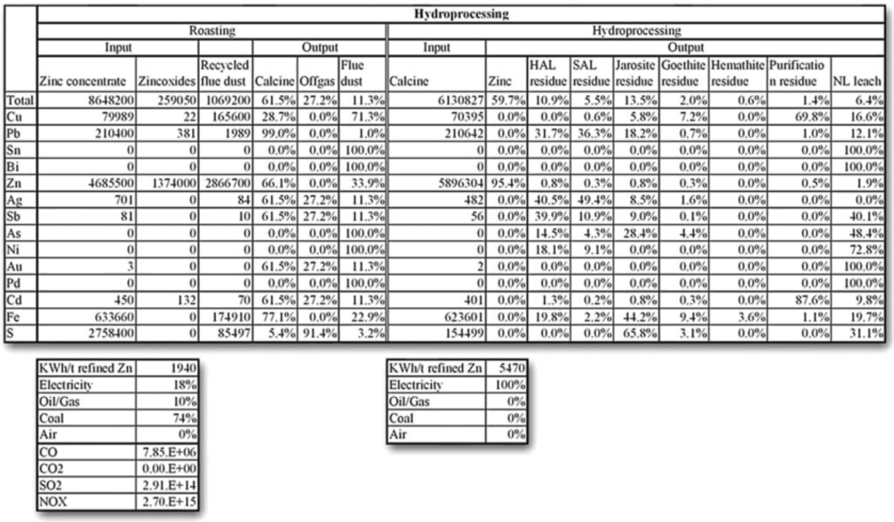
	Imperial Smelter Process																
	Sintering							Smelting						Destillation			
	Input			Output				Input	Output					Input	Output		
	Lead concentrate	Zinc Concentrate	Oxides	Flux	Calcine	Offgas	Flue dust	Calcine	Crude zinc	Lead bullion	Flue dust	Offgas	Slag	Crude zinc	Zinc	Cadmium intermediate	Residue
Total	857000	2162100	104970	9.5%	71.5%	23.5%	14.5%	2233710	40.6%	20.7%	3.6%	1.4%	33.6%	907745	97.9%	0.2%	1.9%
Cu	15125	19997	0	0.0%	99.0%	0.0%	1.0%	34771	2.3%	60.1%	0.6%	0.0%	37.0%	790	0.0%	0.0%	100.0%
Pb	523950	52599	0	0.0%	81.0%	0.0%	19.0%	467005	3.0%	93.6%	3.2%	0.0%	0.2%	14177	0.1%	0.0%	99.9%
Sn	0	0	0	0.0%	81.0%	0.0%	19.0%	0	1.1%	84.2%	12.6%	0.0%	2.1%	0	0.0%	0.0%	100.0%
Bi	1894	0	0	0.0%	81.0%	0.0%	19.0%	1534	1.5%	93.3%	0.4%	0.1%	4.7%	23	0.0%	0.0%	100.0%
Zn	44190	1171400	11671	0.0%	100.0%	0.0%	0.0%	1227261	90.8%	0.0%	3.8%	0.0%	5.3%	1114398	99.6%	0.0%	0.4%
Ag	20396	175	0	0.0%	81.0%	0.0%	19.0%	16663	3.0%	93.6%	3.2%	0.0%	0.2%	506	0.0%	0.0%	100.0%
Sb	10786	20	0	0.0%	25.0%	1.0%	74.0%	2702	0.3%	99.5%	0.0%	0.0%	0.1%	8	0.0%	0.0%	100.0%
As	0	0	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	100.0%
Ni	0	0	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	100.0%
Au	2	1	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	100.0%
Pd	0	0	0	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	100.0%	0	0.0%	0.0%	100.0%
Cd	0	113	0	0.0%	33.0%	0.0%	67.0%	37	94.7%	0.2%	4.8%	0.0%	0.3%	35	0.4%	74.6%	25.0%
Fe	24236	158410	0	0.0%	100.0%	0.0%	0.0%	182646	0.3%	0.2%	0.0%	0.0%	99.4%	594	1.3%	0.0%	98.7%
S	118250	589600	0	0.0%	2.0%	95.0%	3.0%	14157	0.0%	5.7%	3.4%	73.6%	17.3%	3	0.0%	0.0%	100.0%

KWh/t refined Zn	1390
Electricity	80%
Oil/Gas	20%
Coal	0%
Air	0%
CO	0.00.E+00
CO2	0.00.E+00
SO2	7.66.E+07
NOX	2.73.E+09

KWh/t refined Zn	11100
Electricity	11%
Oil/Gas	6%
Coal	83%
Air	0%
CO	2.72.E+08
CO2	3.51.E+08
SO2	7.11.E+06
NOX	8.17.E+08

KWh/t refined Zn	1940
Electricity	11%
Oil/Gas	6%
Coal	83%
Air	0%

Figure B.54: Data refers to recovery % in Imperial Smelting in Figure B.52

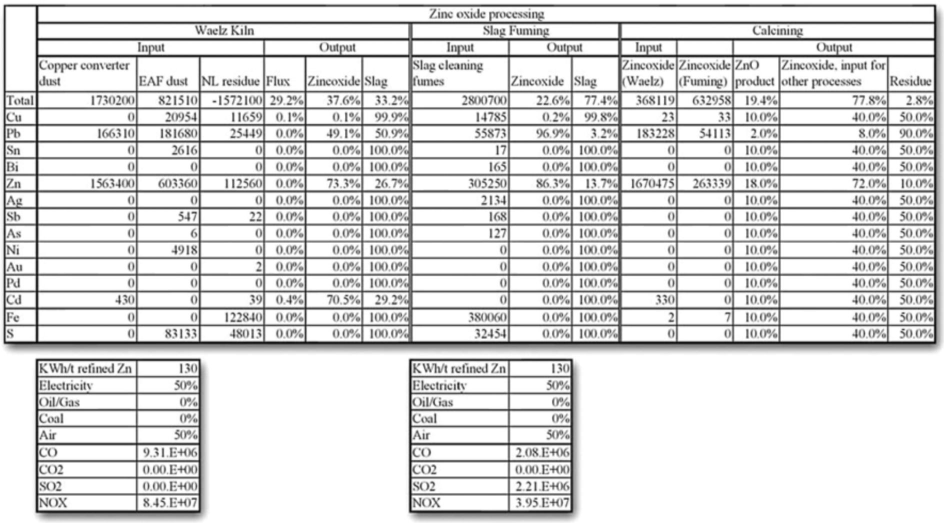


	Hydroprocessing														
	Roasting						Hydroprocessing								
	Input			Output			Input	Output							
	Zinc concentrate	Zincoxides	Recycled flue dust	Calcine	Offgas	Flue dust	Calcine	Zinc	HAL residue	SAL residue	Jarosite residue	Goethite residue	Hemathite residue	Purification residue	NL leach
Total	8648200	259050	1069200	61.5%	27.2%	11.3%	6130827	59.7%	10.9%	5.5%	13.5%	2.0%	0.6%	1.4%	6.4%
Cu	79989	22	165600	28.7%	0.0%	71.3%	70395	0.0%	0.0%	0.6%	5.8%	7.2%	0.0%	69.8%	16.6%
Pb	210400	381	1989	99.0%	0.0%	1.0%	210642	0.0%	31.7%	36.3%	18.2%	0.7%	0.0%	1.0%	12.1%
Sn	0	0	0	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	100.0%
Bi	0	0	0	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	100.0%
Zn	4685500	1374000	2866700	66.1%	0.0%	33.9%	5896304	95.4%	0.8%	0.3%	0.8%	0.3%	0.0%	0.5%	1.9%
Ag	701	0	84	61.5%	27.2%	11.3%	482	0.0%	40.5%	49.4%	8.5%	1.6%	0.0%	0.0%	0.0%
Sb	81	0	10	61.5%	27.2%	11.3%	56	0.0%	39.9%	10.9%	9.0%	0.1%	0.0%	0.0%	40.1%
As	0	0	0	0.0%	0.0%	100.0%	0	0.0%	14.5%	4.3%	28.4%	4.4%	0.0%	0.0%	48.4%
Ni	0	0	0	0.0%	0.0%	100.0%	0	0.0%	18.1%	9.1%	0.0%	0.0%	0.0%	0.0%	72.8%
Au	3	0	0	61.5%	27.2%	11.3%	2	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	100.0%
Pd	0	0	0	0.0%	0.0%	100.0%	0	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	100.0%
Cd	450	132	70	61.5%	27.2%	11.3%	401	0.0%	1.3%	0.2%	0.8%	0.3%	0.0%	87.6%	9.8%
Fe	633660	0	174910	77.1%	0.0%	22.9%	623601	0.0%	19.8%	2.2%	44.2%	9.4%	3.6%	1.1%	19.7%
S	2758400	0	85497	5.4%	91.4%	3.2%	154499	0.0%	0.0%	0.0%	65.8%	3.1%	0.0%	0.0%	31.1%

KWh/t refined Zn	1940
Electricity	18%
Oil/Gas	10%
Coal	74%
Air	0%
CO	7.85.E+06
CO2	0.00.E+00
SO2	2.91.E+14
NOX	2.70.E+15

KWh/t refined Zn	5470
Electricity	100%
Oil/Gas	0%
Coal	0%
Air	0%

Figure B.55: Data refers to recovery % in Hydrometallurgy of zinc in Figure B.52



	Zinc oxide processing													
	Waelz Kiln						Slag Fuming			Calcining				
	Input			Output			Input	Output		Input		Output		
	Copper converter dust	EAF dust	NL residue	Flux	Zincoxide	Slag	Slag cleaning fumes	Zincoxide	Slag	Zincoxide (Waelz)	Zincoxide (Fuming)	ZnO product	Zincoxide, input for other processes	Residue
Total	1730200	821510	-1572100	29.2%	37.6%	33.2%	2800700	22.6%	77.4%	368119	632958	19.4%	77.8%	2.8%
Cu	0	20954	11659	0.1%	0.1%	99.9%	14785	0.2%	99.8%	23	33	10.0%	40.0%	50.0%
Pb	166310	181680	25449	0.0%	49.1%	50.9%	55873	96.9%	3.2%	183228	54113	2.0%	8.0%	90.0%
Sn	0	2616	0	0.0%	0.0%	100.0%	17	0.0%	100.0%	0	0	10.0%	40.0%	50.0%
Bi	0	0	0	0.0%	0.0%	100.0%	165	0.0%	100.0%	0	0	10.0%	40.0%	50.0%
Zn	1563400	603360	112560	0.0%	73.3%	26.7%	305250	86.3%	13.7%	1670475	263339	18.0%	72.0%	10.0%
Ag	0	0	0	0.0%	0.0%	100.0%	2134	0.0%	100.0%	0	0	10.0%	40.0%	50.0%
Sb	0	547	22	0.0%	0.0%	100.0%	168	0.0%	100.0%	0	0	10.0%	40.0%	50.0%
As	0	6	0	0.0%	0.0%	100.0%	127	0.0%	100.0%	0	0	10.0%	40.0%	50.0%
Ni	0	4918	0	0.0%	0.0%	100.0%	0	0.0%	100.0%	0	0	10.0%	40.0%	50.0%
Au	0	0	2	0.0%	0.0%	100.0%	0	0.0%	100.0%	0	0	10.0%	40.0%	50.0%
Pd	0	0	0	0.0%	0.0%	100.0%	0	0.0%	100.0%	0	0	10.0%	40.0%	50.0%
Cd	430	0	39	0.4%	70.5%	29.2%	0	0.0%	100.0%	330	0	10.0%	40.0%	50.0%
Fe	0	0	122840	0.0%	0.0%	100.0%	380060	0.0%	100.0%	2	7	10.0%	40.0%	50.0%
S	0	83133	48013	0.0%	0.0%	100.0%	32454	0.0%	100.0%	0	0	10.0%	40.0%	50.0%

KWh/t refined Zn	130
Electricity	50%
Oil/Gas	0%
Coal	0%
Air	50%
CO	9.31.E+06
CO2	0.00.E+00
SO2	0.00.E+00
NOX	8.45.E+07

KWh/t refined Zn	130
Electricity	50%
Oil/Gas	0%
Coal	0%
Air	50%
CO	2.08.E+06
CO2	0.00.E+00
SO2	2.21.E+06
NOX	3.95.E+07

Figure B.56: Data refers to recovery % in zinc oxide processing and hence recycling in Figure B.52

B.10 Calculation waste composition

B.10.1 Method

In the modelling of waste flows from consumption stocks, [147] suggest to model the stock as a "time buffer". Metals in use (economic stocks) and waste generation can then be approximated using general metal statistics that report on the different end uses of metals as function of time, and estimates of life span distributions for these end uses or rather end use categories (A1 in Figure B.57). The total economic stocks of metals can than be determined by integration over the longest life span. The actual composition of the old scrap from separation processes can be estimated (A2 in Figure B.57) similarly by partitioning the end use categories to standardized routes for typical waste categories (Municipal Solid Waste, Wasted Electric and Electronic Equipment or End-of-Life Vehicles etc.). The data on the manufacture, consumption and solid waste management stages is given below.

B.10.2 Consumption

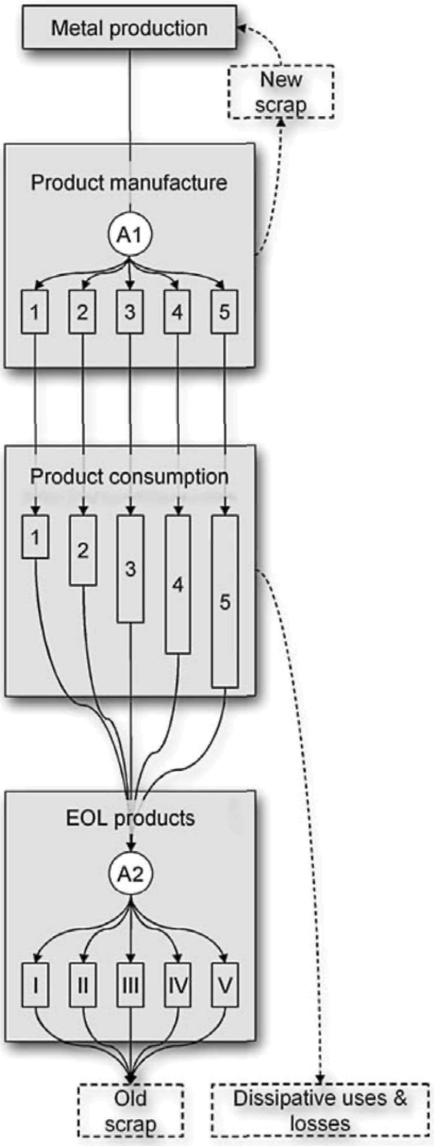


Figure B.57: Estimation of metals in stock and waste generation using metal statistics on the different end uses of metals

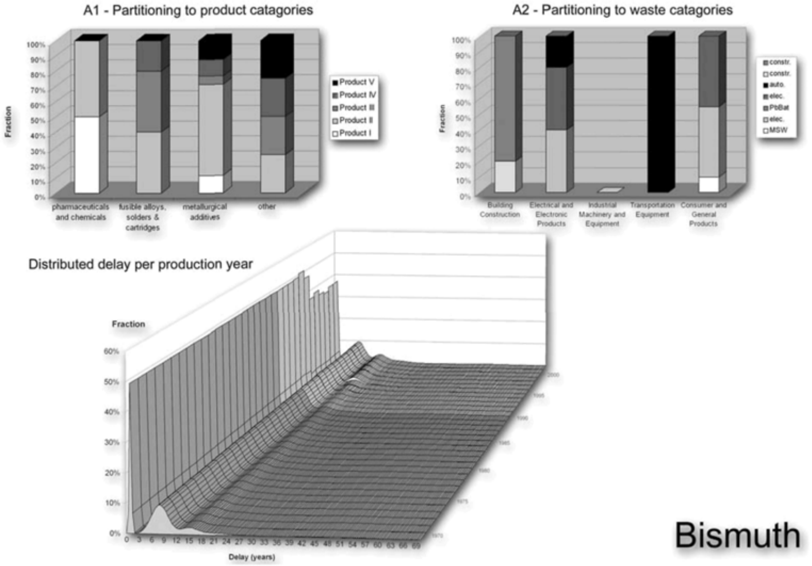


Figure B.58: Partitioning of Bi between product and waste and also the definition of the delays before these are returned

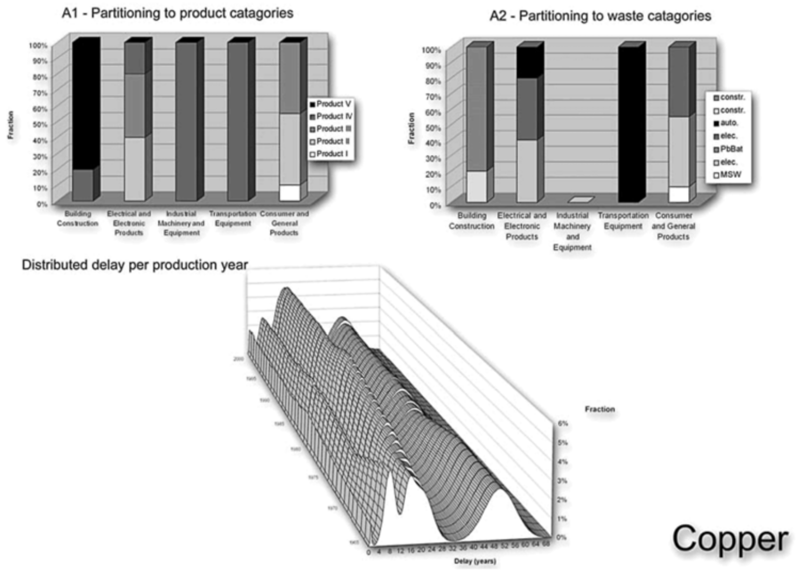


Figure B.59: Partitioning of Cu between product and waste and also the definition of the delays before these are returned

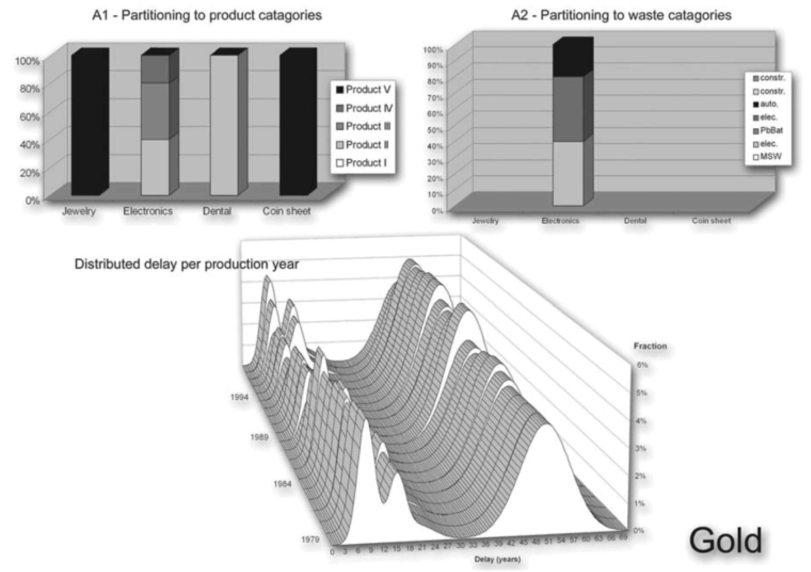


Figure B.60: Partitioning of Au between product and waste and also the definition of the delays before these are returned

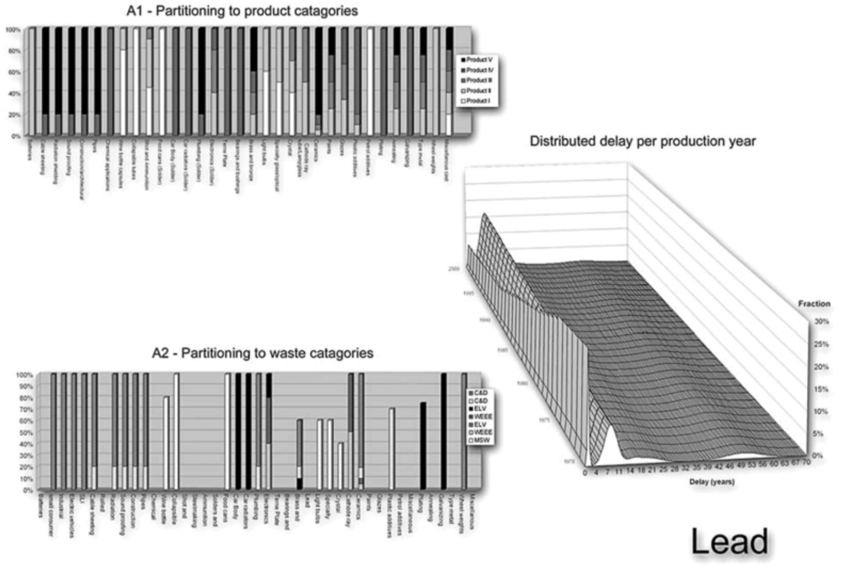


Figure B.61: Partitioning of Pb between product and waste and also the definition of the delays before these are returned

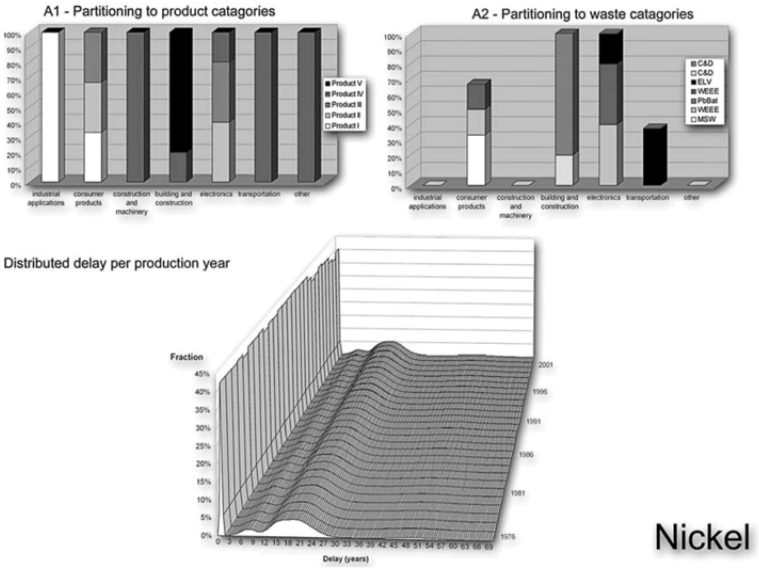


Figure B.62: Partitioning of Ni between product and waste and also the definition of the delays before these are returned

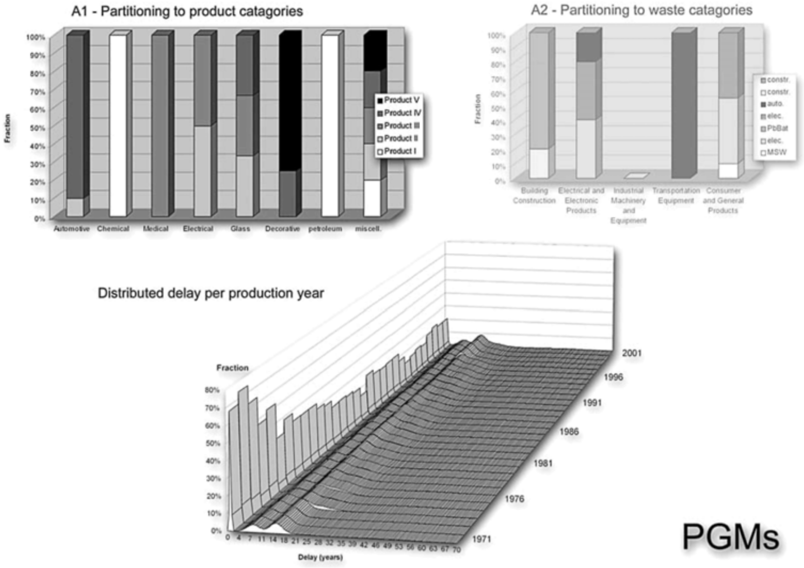


Figure B.63: Partitioning of PGM's between product and waste and also the definition of the delays before these are returned

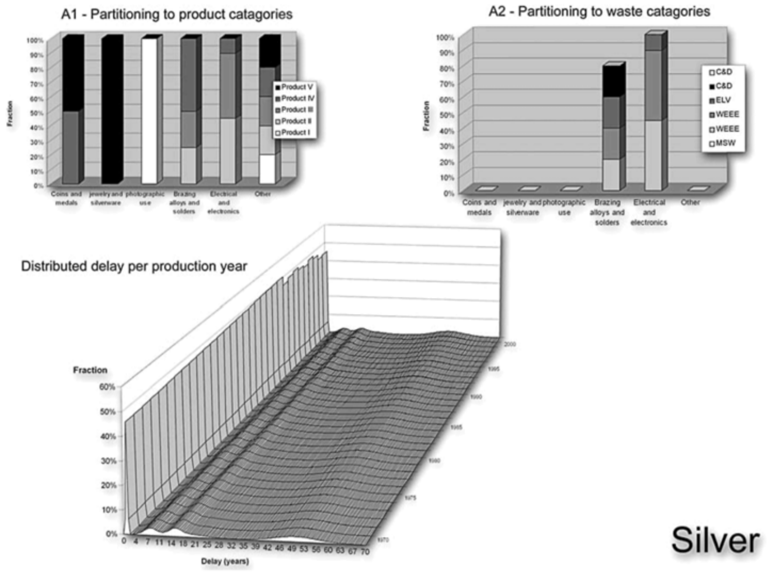


Figure B.64: Partitioning of Ag between product and waste and also the definition of the delays before these are returned

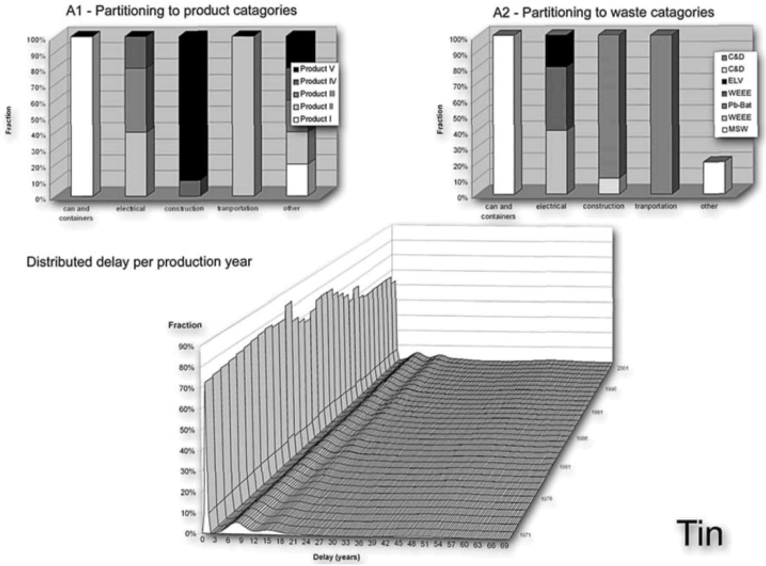


Figure B.65: Partitioning of Sn between product and waste and also the definition of the delays before these are returned

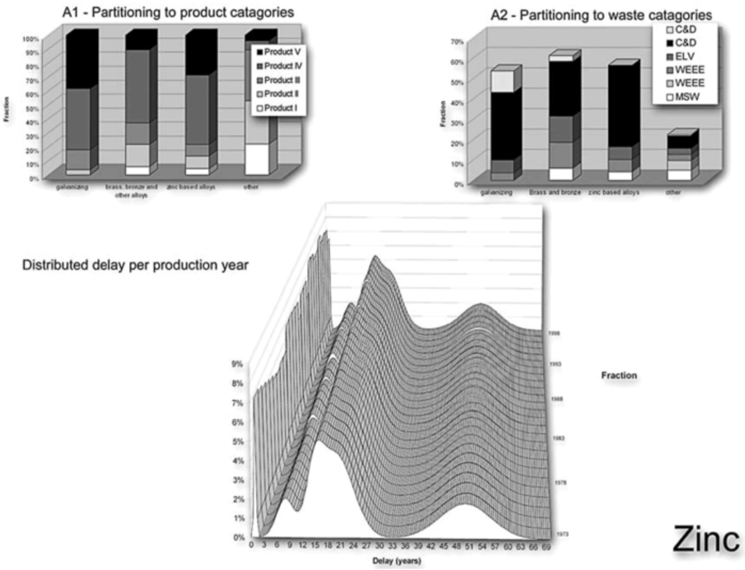


Figure B.66: Partitioning of Zn between product and waste and also the definition of the delays before these are returned

B.10.3 Solid waste management

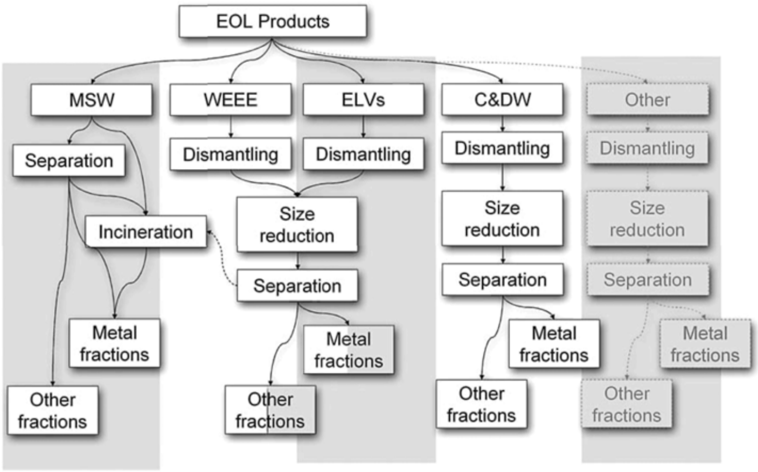


Figure B.67: Simplified solid waste management flowchart

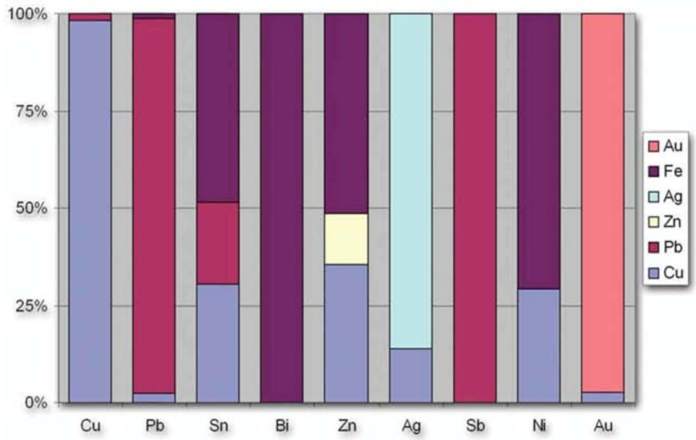
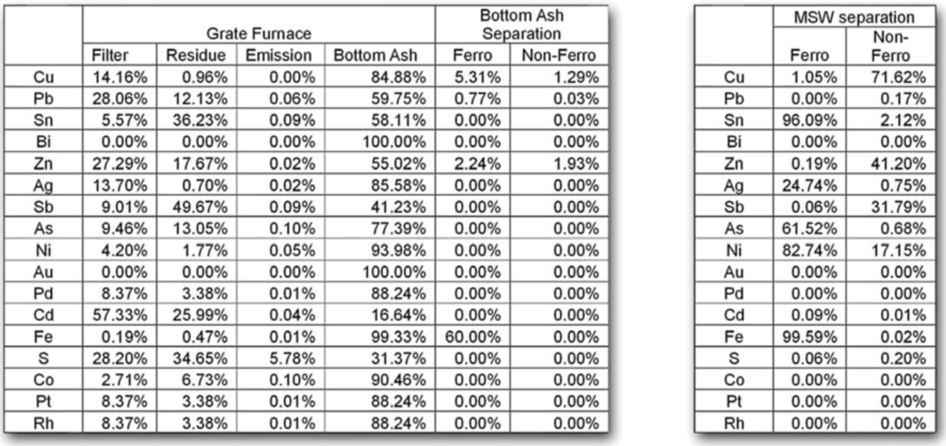


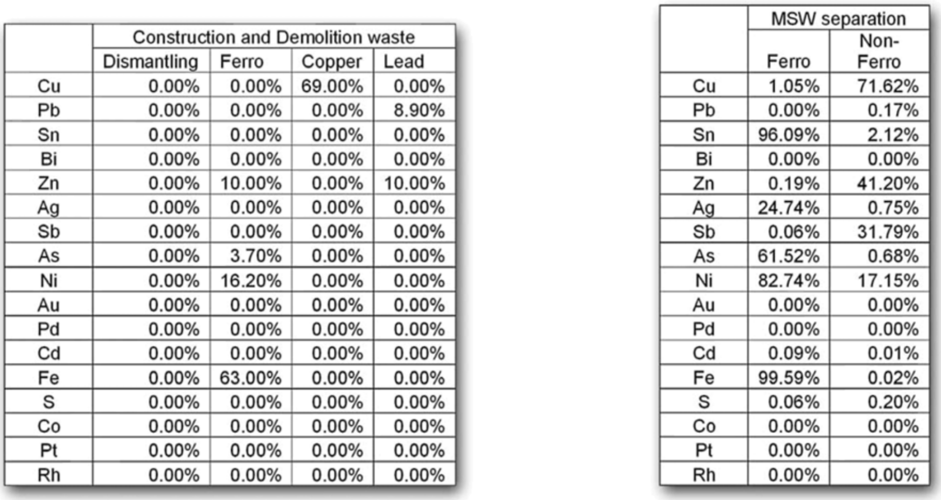
Figure B.68: Partitioning of "other" waste to carrier metals: Au, Fe, Ag, Zn, Pb and Cu



	Grate Furnace				Bottom Ash Separation	
	Filter	Residue	Emission	Bottom Ash	Ferro	Non-Ferro
Cu	14.16%	0.96%	0.00%	84.88%	5.31%	1.29%
Pb	28.06%	12.13%	0.06%	59.75%	0.77%	0.03%
Sn	5.57%	36.23%	0.09%	58.11%	0.00%	0.00%
Bi	0.00%	0.00%	0.00%	100.00%	0.00%	0.00%
Zn	27.29%	17.67%	0.02%	55.02%	2.24%	1.93%
Ag	13.70%	0.70%	0.02%	85.58%	0.00%	0.00%
Sb	9.01%	49.67%	0.09%	41.23%	0.00%	0.00%
As	9.46%	13.05%	0.10%	77.39%	0.00%	0.00%
Ni	4.20%	1.77%	0.05%	93.98%	0.00%	0.00%
Au	0.00%	0.00%	0.00%	100.00%	0.00%	0.00%
Pd	8.37%	3.38%	0.01%	88.24%	0.00%	0.00%
Cd	57.33%	25.99%	0.04%	16.64%	0.00%	0.00%
Fe	0.19%	0.47%	0.01%	99.33%	60.00%	0.00%
S	28.20%	34.65%	5.78%	31.37%	0.00%	0.00%
Co	2.71%	6.73%	0.10%	90.46%	0.00%	0.00%
Pt	8.37%	3.38%	0.01%	88.24%	0.00%	0.00%
Rh	8.37%	3.38%	0.01%	88.24%	0.00%	0.00%

	MSW separation	
	Ferro	Non-Ferro
Cu	1.05%	71.62%
Pb	0.00%	0.17%
Sn	96.09%	2.12%
Bi	0.00%	0.00%
Zn	0.19%	41.20%
Ag	24.74%	0.75%
Sb	0.06%	31.79%
As	61.52%	0.68%
Ni	82.74%	17.15%
Au	0.00%	0.00%
Pd	0.00%	0.00%
Cd	0.09%	0.01%
Fe	99.59%	0.02%
S	0.06%	0.20%
Co	0.00%	0.00%
Pt	0.00%	0.00%
Rh	0.00%	0.00%

Figure B.69: Distribution of materials in a grate waste incinerator



	Construction and Demolition waste			
	Dismantling	Ferro	Copper	Lead
Cu	0.00%	0.00%	69.00%	0.00%
Pb	0.00%	0.00%	0.00%	8.90%
Sn	0.00%	0.00%	0.00%	0.00%
Bi	0.00%	0.00%	0.00%	0.00%
Zn	0.00%	10.00%	0.00%	10.00%
Ag	0.00%	0.00%	0.00%	0.00%
Sb	0.00%	0.00%	0.00%	0.00%
As	0.00%	3.70%	0.00%	0.00%
Ni	0.00%	16.20%	0.00%	0.00%
Au	0.00%	0.00%	0.00%	0.00%
Pd	0.00%	0.00%	0.00%	0.00%
Cd	0.00%	0.00%	0.00%	0.00%
Fe	0.00%	63.00%	0.00%	0.00%
S	0.00%	0.00%	0.00%	0.00%
Co	0.00%	0.00%	0.00%	0.00%
Pt	0.00%	0.00%	0.00%	0.00%
Rh	0.00%	0.00%	0.00%	0.00%

	MSW separation	
	Ferro	Non-Ferro
Cu	1.05%	71.62%
Pb	0.00%	0.17%
Sn	96.09%	2.12%
Bi	0.00%	0.00%
Zn	0.19%	41.20%
Ag	24.74%	0.75%
Sb	0.06%	31.79%
As	61.52%	0.68%
Ni	82.74%	17.15%
Au	0.00%	0.00%
Pd	0.00%	0.00%
Cd	0.09%	0.01%
Fe	99.59%	0.02%
S	0.06%	0.20%
Co	0.00%	0.00%
Pt	0.00%	0.00%
Rh	0.00%	0.00%

Figure B.70: Distribution of construction and demolition waste materials

Appendix C

Car recycling - a numerical study

C.1 Matlab Source code for Dynamic Model

Use Matlab's Simulink and run the "*.m" flies provided on the CD rom under the directory "**MATLAB**". This example serves as an illustration how the models in Part III were solved and should be used as a basis to improve and build own models.

```
%===================================================================================
%Aluminium recycling (c) MAR&AvS 2002-2003
%===================================================================================
%WEIBULL DISTRIBUTION (NORMALISED) WITH VARIOUS FEED FUNCTIONS
%Parameters can skew data at will
%Feed function can be changed
%===================================================================================
clc;   %Clear screen
clear; %Clear all variables.  Always do this to ensure that nothing undue
        %affects the simulations.
%Global variables used also in function. Must be defined here and in function 'cycles'
global PRODUCTION CARSLEAVING CARSLEAVING_RECYCLED OUTFLOW
%Initializing variables
YEAR_PRODUCTION  = 20;
YEAR_DISMANTLING = 20;  %Total simulation years / i.e. related to year of dismantling
WEIGHT_CLASS     = 20;  %Weight classes
MASS_PERCENTAGE  = 40;  %Mass percentage classes of element in car

%Initializing matrices for age of car
for ii  =  1:YEAR_PRODUCTION     %Production year is 'ii'
   for i = 1:2*YEAR_DISMANTLING  %Dismantling Year is 'i'
      A(i,ii) = 0; AA(i,ii) = 0; AAA(i,ii) = 0;
   end
end
%Initializing matrices for weight of car
for ii  =  1:YEAR_PRODUCTION     %Production year is 'ii'
   for w = 1:WEIGHT_CLASS        %Weight class is 'w'
      B(w,ii) = 0; BB(w,ii) = 0; BBB(w,ii) = 0;
```

```
   end
end
%Initializing matrices for mass percentage/time of car
for w = 1:WEIGHT_CLASS              %Weight class is 'w'
   for ii  =  1:YEAR_PRODUCTION     %Production year is 'ii'
      for mp = 1:MASS_PERCENTAGE    %Mass percentage is 'mp'
         C(mp,ii) = 0; CC(w,mp,ii) = 0; CCC(w,mp,ii) = 0;
      end
   end
end
%==================================================================================
%All functions for age distribution
%==================================================================================
%WEIBULL distribution variables.

ALPHA = 6.8;
BETA = 14;
%Cars normalised under the DISTRIBUTIONS.
for ii = 1:YEAR_PRODUCTION       %Year of production
   for i = 1:YEAR_DISMANTLING    %Year of dismantling
      AAA(i,ii) = (ALPHA/BETA)*((i/BETA)^(ALPHA-1))*exp(-((i/BETA)^ALPHA));
   end
end
%==================================================================================
%All function for weight distribution
%==================================================================================
%WEIBULL distribution variables
for ii=1:YEAR_PRODUCTION
   ALPHA(ii) = 3.1 + 0.05*(ii-1);
   BETA(ii)  = 5.1 + 0.2*(ii-1);
end
%Definition of masses in weight classes
for w=1:WEIGHT_CLASS
   WEIGHT_CLASS_MASS(w)=500+(w-1)*100;
end
%Weibull distribution
for ii = 1:YEAR_PRODUCTION       %Year of production
   for w = 1:WEIGHT_CLASS        %Weight class
      BBB(w,ii) = (ALPHA(ii)/BETA(ii))*((w/BETA(ii))^(ALPHA(ii)-1))
                  *exp(-(w/BETA(ii))^ALPHA(ii));
   end
end
%==================================================================================
%All function for mass percentage/year of production distribution for each of the
%weight classes
%==================================================================================
%WEIBULL distribution variables.  The chosen ALPHA and BETA give a skew function to
%the high years. ALPHA and BETA an be changed to change the skewness. ALPHA(w) and
%BETA(w) determine the different shape of the distribution function for the
```

```
%different weight classes w
for w = 1:WEIGHT_CLASS
   ALPHA(w)=5+4*(w/WEIGHT_CLASS);
   BETA(w) =6+2*(w/WEIGHT_CLASS);
end
%Definition of aluminium percentages
Al_MAX=10; %Maximum percentage of Aluminium
for mp=1:MASS_PERCENTAGE
   M_Al(mp) = mp*(Al_MAX/MASS_PERCENTAGE); %/MASS_PERCENTAGE);
end
%Weibull distribution (year of production and mass percentage of aluminium for each
%weight class)
for w = 1:WEIGHT_CLASS              %Weight class
   for ii = 1:YEAR_PRODUCTION       %Year of production
      for mp = 1:MASS_PERCENTAGE    %Mass percentage of aluminium
         CCC(w,mp,ii) = (ALPHA(w)/BETA(w))*((M_Al(mp)/BETA(w))^(ALPHA(w)-1))
                        *exp(-((M_Al(mp)/BETA(w))^ALPHA(w)));
      end
   end
end
%--------------------------------------------------------------------------------
%Integration of age distribution
for ii=1:YEAR_PRODUCTION       %Year of production
   sum=0;
   for i=1:YEAR_DISMANTLING-1  %Year of dismantling
      AA(i,ii)=( AAA(i,ii) + AAA(i+1,ii) )*1/2;
      sum=sum+AA(i,ii);
   end
end
sum
pause;
%Filling matrix with number of cars between a time increment.
for ii=1:YEAR_PRODUCTION         %Year of production
   for i=1:YEAR_DISMANTLING      %Year of dismantling
      A(ii+i-1,ii)=AA(i,ii);     %Creating the shifted distribution.
   end
end
%Integration of weight distribution
for ii=1:YEAR_PRODUCTION         %Year of production
   sum1=0;
   for w=1:WEIGHT_CLASS-1        %Weight class
      BB(w,ii)=( BBB(w,ii) + BBB(w+1,ii) )*1/2;
      sum1=sum1+BB(w,ii);
   end
   sum1
end
pause;
%Integration of mass percentage of Al distribution
for w = 1:WEIGHT_CLASS              %Weight class
```

```
   for ii=1:YEAR_PRODUCTION          %Year of production
      %sum=0;
      for mp=1:MASS_PERCENTAGE-1    %Mass percentage
         CC(w,mp,ii)=( CCC(w,mp,ii) + CCC(w,mp+1,ii) )*(Al_MAX/MASS_PERCENTAGE)/2;
         %sum=sum+CC(w,mp,ii);
      end
   end
end
%sum
%pause;
delete 'AlAv1102';
%Average mass percentage of Al
for w =1:WEIGHT_CLASS                %Weight class
   for ii=1:YEAR_PRODUCTION          %Year of production
      Al_AVERAGE(w,ii) = 0;
      for mp=1:MASS_PERCENTAGE-1     %Mass percentage
         Al_AVERAGE(w,ii)=Al_AVERAGE(w,ii) + M_Al(mp)*CC(w,mp,ii)/100;
      end
   end
end
Al_AVERAGE
pause;
save AlAv1102 Al_AVERAGE -ascii;
close;
map = [0 0 0];
%Plotting of age graph with Matlab functions
axis([0 2*YEAR_DISMANTLING 0 YEAR_PRODUCTION 0 YEAR_PRODUCTION]);
%MATLAB function for plotting 3D age distribution
colormap(map);
mesh(A);
title('Distribution of number of cars');
xlabel('Year of Production');
ylabel('Year of Dismantling');
zlabel('Frequency of the number of cars');
pause;
close;
%Plotting of weight graph with Matlab functions
axis([0 WEIGHT_CLASS 0 YEAR_PRODUCTION 0 YEAR_PRODUCTION]);
%MATLAB function for plotting 3D weight distribution
colormap(map);
mesh(BBB);
%title('Distribution of weight of cars for different Years of Production');
xlabel('Year of Production');
ylabel('Weight class');
zlabel('Frequency of the number of cars');
pause;
close;
%for w = 1:WEIGHT_CLASS               %Weight class
%   for ii=1:YEAR_PRODUCTION          %Year of production
```

```
%      for mp=1:MASS_PERCENTAGE-1     %Mass percentage
%         C(mp,ii)=CC(w,mp,ii);
%      end
%   end
%Plotting of mass percentage/time graph with Matlab functions
%   axis([0 Al_MAX 0 YEAR_PRODUCTION 0 YEAR_PRODUCTION]);
%   axis tight;
%MATLAB function for plotting 3D mass percentage distribution
%   mesh(C);
%   title('Distribution of mass percentage of Al in cars for different Years of
%   Production');   xlabel('Year of Production');
%   ylabel('Al Mass percentage class');
%   zlabel('Frequency');
%   w
%   pause;
%   close;
%end
%close;
%Recyclingrate Al cast, variable, given by optimization model
RECYCLINGRATE(1)    = 0.5;  RECYCLINGRATE(2)    = 0.5;  RECYCLINGRATE(3)    = 0.5;
RECYCLINGRATE(4)    = 0.5;  RECYCLINGRATE(5)    = 0.5;  RECYCLINGRATE(6)    = 0.5;
RECYCLINGRATE(7)    = 0.5;  RECYCLINGRATE(8)    = 0.5;  RECYCLINGRATE(9)    = 0.5;
RECYCLINGRATE(10)   = 0.5;  RECYCLINGRATE(11)   = 0.5;  RECYCLINGRATE(12)   = 0.5;
RECYCLINGRATE(13)   = 0.5;  RECYCLINGRATE(14)   = 0.5;  RECYCLINGRATE(15)   = 0.5;
RECYCLINGRATE(16)   = 0.5;  RECYCLINGRATE(17)   = 0.5;  RECYCLINGRATE(18)   = 0.5;
RECYCLINGRATE(19)   = 0.5;  RECYCLINGRATE(20)   = 0.5;
%Production function
for ii=1:YEAR_PRODUCTION
  TOTAL_CAR(ii)=1000000;
end
%Feed function for weight of car based on weight distribution
for ii=1:YEAR_PRODUCTION
   TOTAL_PRODUCT_CAR(ii)=0;
   for w=1:WEIGHT_CLASS
      TOTAL_PRODUCT_CAR(ii)=TOTAL_PRODUCT_CAR(ii) + TOTAL_CAR(ii)*BB(w,ii)
                            *WEIGHT_CLASS_MASS(w);
   end
   %TOTAL_PRODUCT_CAR(ii)
   %pause;
end
%Feed function for component based on weight distribution and mass percentage
%distribution
for ii=1:YEAR_PRODUCTION
   TOTAL_PRODUCT(ii)=0;
   for w=1:WEIGHT_CLASS
      TOTAL_PRODUCT(ii)=TOTAL_PRODUCT(ii) + TOTAL_CAR(ii)*BB(w,ii)
                        *WEIGHT_CLASS_MASS(w)*Al_AVERAGE(w,ii);
   end
   %TOTAL_PRODUCT(ii)
```

```
   %pause;
end
%Initializing counting variables
NN                  = 0;
Y0                  = [0.0 0.0 0.0 0.0]'; %Initial vector for differential equation
COLLECTIONRATE             = 0.9;         %Between 0 and 1
DELAY                      = 0;           %Years delay for recycling of Al
OUTFLOW                    = 1;
FRACTION_RETURNING_TO_CAR_CYCLE= 0.9;
for ii=1:YEAR_PRODUCTION
   SECONDARY_PRODUCT(ii) = 0;
end
delete 'sim1102'
delete 'sim1202'
%ODE23 solution=====================================================================
for TFINAL = 1:YEAR_DISMANTLING %Simulation time i.e. up to
                                %the year of dismantling 'i'
   %Summing weight of car over all production years for dismantling year TFINAL
   CARSLEAVING_W = 0;
   for ii=1:YEAR_PRODUCTION      % ii Production year! TFINAL Dismantling year!
      CARSLEAVING_W = CARSLEAVING_W + ( TOTAL_PRODUCT_CAR(ii) )*A(TFINAL,ii);
   end
   %Summing weight of component over all production years for dismantling year TFINAL
   CARSLEAVING = 0;
   for ii=1:YEAR_PRODUCTION      % ii Production year! TFINAL Dismantling year!
      CARSLEAVING = CARSLEAVING + ( TOTAL_PRODUCT(ii) )*A(TFINAL,ii);
   end
   %Summing amount of cars over all production years for dismantling year TFINAL
   CARSLEAVING_CAR = 0;
   for ii=1:YEAR_PRODUCTION      % ii Production year! TFINAL Dismantling year!
      CARSLEAVING_CAR = CARSLEAVING_CAR + TOTAL_CAR(ii)*A(TFINAL,ii);
   end
   WEIGHT = CARSLEAVING/CARSLEAVING_CAR; %Weight of the component (aluminium) in
                                         %average car in year of dismantling TFINAL
   %WEIGHT
   %pause;
   WEIGHT_CAR = CARSLEAVING_W/CARSLEAVING_CAR; %Weight of the average car in year
                                               %of dismantling TFINAL
   %WEIGHT_CAR
   %pause;
   MP_CAR=WEIGHT/WEIGHT_CAR; %Mass percentage of component (aluminium) in average
                             %car in year of dismantling TFINAL
   %MP_CAR
   %pause;
   %Creating matrices for plotting data
   X_ALL(TFINAL,1) = WEIGHT;
   X_ALL(TFINAL,2) = WEIGHT_CAR;
   X_ALL(TFINAL,3) = MP_CAR;
   CARSLEAVING1 = CARSLEAVING*COLLECTIONRATE;
```

```
   %Recycling stream with years time delay included
   CARSLEAVING_MATRIX(TFINAL) = CARSLEAVING1*RECYCLINGRATE(TFINAL);
   if (TFINAL-DELAY)>0
      CARSLEAVING_RECYCLED = CARSLEAVING_MATRIX(TFINAL-DELAY);
   else
      CARSLEAVING_RECYCLED = 0;
   end
   %Summing all cars over all production years for all years up to year TFINAL
   %CARSLEAVING_CUMULATIVE(TFINAL)=0;
   if TFINAL>1
      CARSLEAVING_CUMULATIVE(TFINAL) = CARSLEAVING_CUMULATIVE(TFINAL-1)
                                     + CARSLEAVING;
   else
      CARSLEAVING_CUMULATIVE(TFINAL) = CARSLEAVING;
   end
   %Cars produced in a year=========================================================
   PRODUCTION = (TOTAL_PRODUCT(TFINAL));
   %Car production stops after 20 years (Change this value if required to 0 or any
   %other value.)
   if TFINAL > 20
      %PRODUCTION=0;
      PRODUCTION = (TOTAL_PRODUCT(TFINAL));
   end
   %================================================================================
   %Solving differential equation in function 'cycles_all.m' between two successive
   %years
   [T,Y] = ode23('cycles_all',[TFINAL-1 TFINAL*(1+eps)],Y0);
   Y0 = [ Y(length(Y),1) Y(length(Y),2)  Y(length(Y),3) Y(length(Y),4)];
   for N = 1: length(Y)
      YY(NN+N) = Y(N,2);
      TT(NN+N) = T(N);
   end
   NN = NN + length(Y);
   SECONDARY_PRODUCT(TFINAL+1)=Y(length(Y),4)*OUTFLOW*FRACTION_RETURNING_TO_CAR_CYCLE;
   %Creating matrices for plotting data
   T_ALL(TFINAL)   = TFINAL;
   Y_ALL(1,TFINAL) = CARSLEAVING_CUMULATIVE(TFINAL);
   Y_ALL(2,TFINAL) = CARSLEAVING;
   Y_ALL(3,TFINAL) = Y(N,1);                          %PRODUCT_CUMULATIVE(TFINAL);
   Y_ALL(4,TFINAL) = PRODUCTION;
   Y_ALL(5,TFINAL) = Y(N,2);
   Y_ALL(6,TFINAL) = Y(N,3);
   Y_ALL(7,TFINAL) = Y(N,4);
   Y_ALL(8,TFINAL) = CARSLEAVING_CAR;
end
for i = 1:YEAR_DISMANTLING
   Y1(i)=Y_ALL(1,i); Y2(i)=Y_ALL(2,i); Y3(i)=Y_ALL(3,i);
   Y4(i)=Y_ALL(4,i); Y5(i)=Y_ALL(5,i); Y6(i)=Y_ALL(6,i);
   Y7(i)=Y_ALL(7,i);Y8(i)=Y_ALL(8,i);
```

```
end
save sim1102 X_ALL -ascii;
save sim1202 Y_ALL -ascii;
%Drawing figure for total aluminium cars : normal scale
plot(T_ALL,Y1,'gx-',T_ALL,Y2,'md-',T_ALL,Y3,'ro-',T_ALL,Y4,'c<-',T_ALL,Y5,'bh-')
%title('Change of total number of cars');
axis([0 20 0 1600000000]);
xlabel('Year of dismantling');
ylabel('Mass (kg)');
legend('Cumulative Al in cars leaving (kg)','Yearly Al in cars leaving (kg)',
'Cumulative production of Al in cars (kg)','Production Al per year (kg)',
'Al in cars left in circulation (kg)',2);
T_ALL(TFINAL)
Y_ALL(1,TFINAL)
Y_ALL(2,TFINAL)
Y_ALL(3,TFINAL)
Y_ALL(4,TFINAL)
Y_ALL(5,TFINAL)
Y_ALL(6,TFINAL)
Y_ALL(7,TFINAL)
Y_ALL(8,TFINAL)
pause;
clc;
%Drawing figure for total aluminium in cars : semilog scale
semilogy(T_ALL,Y1,'gx-',T_ALL,Y2,'md-',T_ALL,Y3,'ro-',T_ALL,Y4,'c<-',T_ALL,Y5,'bh-',
         T_ALL,Y6,'k*-',T_ALL,Y7,'bp--'),
%title('Change of total number of cars');
xlabel('Year of dismantling');
ylabel('Mass cars (kg)');
legend('Cumulative cars leaving (kg)','Yearly cars leaving (kg)','Cumulative
        production of cars (kg)','Production per year (kg)','Cars left in circulation
       (kg)','Recycle mass (kg)','Reservoir output (kg)',4);
pause;
close all; %closes figures
clc;
%Calculation of primary cars
for ii=1:YEAR_PRODUCTION
   PRIMARY_PRODUCT(ii)=0;
   PRIMARY_CARS(ii)=0;
end
for ii=1:YEAR_PRODUCTION
   while (TOTAL_PRODUCT(ii)-PRIMARY_PRODUCT(ii)-SECONDARY_PRODUCT(ii))>=0
      PRIMARY_PRODUCT(ii) = 0;
      PRIMARY_CARS(ii)=PRIMARY_CARS(ii)+1000;
      for w=1:WEIGHT_CLASS
          PRIMARY_PRODUCT(ii)=PRIMARY_PRODUCT(ii)+PRIMARY_CARS(ii)*BB(w,ii)
                              *WEIGHT_CLASS_MASS(w)*Al_AVERAGE(w,ii);
      end
   end
```

```
end
%Calculation of secondary cars
for ii=1:YEAR_PRODUCTION
   CALC_PRODUCT(ii)=0;
   SECONDARY_CARS(ii)=0;
end
for ii=1:YEAR_PRODUCTION
   while (SECONDARY_PRODUCT(ii)-CALC_PRODUCT(ii))>=0
      CALC_PRODUCT(ii) = 0;
      SECONDARY_CARS(ii)=SECONDARY_CARS(ii)+1000;
      for w=1:WEIGHT_CLASS
          CALC_PRODUCT(ii)=CALC_PRODUCT(ii)+SECONDARY_CARS(ii)*BB(w,ii)
                           *WEIGHT_CLASS_MASS(w)*Al_AVERAGE(w,ii);
      end
   end
end
for ii=1:YEAR_PRODUCTION
   PRIMARY_CARS(ii)
   SECONDARY_CARS(ii)
   PRIMARY_CARS(ii)+SECONDARY_CARS(ii)
end
%Drawing figure for total aluminium cars : normal scale
plot(T_ALL,PRIMARY_CARS,'gx-',T_ALL,SECONDARY_CARS,'md-',
     T_ALL,PRIMARY_CARS+SECONDARY_CARS,'bp--'),
%title('Change of total number of cars');
xlabel('Year of production');
ylabel('Number of cars');
legend('Primary cars','Secondary cars',4);
pause;
close all;
clc;
```

C.2 AMPL code for optimization model

The models of Part III of this book can be converted into the syntax required by **A**nother **M**athematical **P**rogramming **L**anguage AMPL. Solving an AMPL model is easy via the internet. At the following www-address, a good on-line solver can presently be found:

- http://www-neos.mcs.anl.gov/neos/solvers/NCO:IPOPT/solver-www.html

In order to get a model solved, 3 different files have to be uploaded to the site:

- a model file (xxx.mod)
- a data file (xxx.dat)
- a commands file (xxx.run).

The first two files are required to define a model, the last one is only important to make the solver display the variables you want to see. Upload the three files, click on 'Submit to NEOS', and wait for the results.**Note:** Please find the data file "*.dat" for this problem under the AMPL directory of the CD rom, it is not listed below due to its length. All the files are under the directory "**AMPL**" on the CD rom. An example is given, which serves as a start for a user to program her/his own model based on the theory given in the book. The user is urged to creatively build new models and expand what we have done with our examples.

```
#
# Created on 04-03-2005 #
# SETS #

set LC;# Liberation Classes (LC1...LC5)
set SC;# particle Size Classes (SC1...SC5)
set MC;# Mineral Classes (MC1...MC5)
set MT;# Material Types (Al wrought, Al cast, Copper, Steel, Rest)
set Pr;# End Products (Aluminium, Copper, Steel, ASR, Rest)

# PARAMETERS #

param MC_Dist{MC}>=0 <=1;# Mineral Classes Distribution;
param LC_Dist{SC,LC}>=0 <=1;# Liberation Classes Distribution;
param LC_Def{MC,LC,MT}>=0 <=1;# Liberation Class Definitions;
param SC_Dist{SC}>=0 <=1;# Size Class Distribution;

param SF_i3_x{SC,MC}>=0 <=1;# Split Factors Air Suction to stream x3
param SF_i4_x{MC,LC}>=0 <=1;# Split Factors Magnetic Separation to stream x4
param SF_i5_x{SC,MC,LC}>=0 <=1;# Split Factors Eddy Current to stream x5
param SF_i5_y{SC,MC,LC}>=0 <=1;# Split Factors Eddy Current to stream y5
param SF_i7_x{SC,MC,LC}>=0 <=1;# Split Factors Non-ferrous 1 to stream x7
param SF_i9_x{SC,MC,LC}>=0 <=1;# Split Factors Non-ferrous 2 to stream x9
param SF_i9_y{SC,MC,LC}>=0 <=1;# Split Factors Non-ferrous 2 to stream yy

param Pr_Matrix_Aluminium{Pr,MC,SC,LC};# Matrix box for Aluminium Product
param Pr_Matrix_Copper{Pr,MC,SC,LC};# Matrix box for Copper Product
param Pr_Matrix_Steel{Pr,MC,SC,LC};# Matrix box for Steel Product
param Pr_Matrix_ASR{Pr,MC,SC,LC};# Matrix box for ASR Product
param Pr_Matrix_Rest{Pr,MC,SC,LC};# Matrix box for Rest Product

param Matrix_Pr_MT{Pr,MT};# Matrix for relation of Material Types with End Products

param Matrix_Metal_Streams{Pr};# Matrix for screening the metal streams out of the End Products


% VARIABLES #

var shred_result_1{MC,MT,SC} >=0 <=1 ; # Result of Shredder calculation, step 1 of 6
var shred_result_2{LC}       >=0 <=1 ; # Result of Shredder calculation, step 2 of 6
var shred_result_3{MC,MT,SC} >=0 <=1 ; # Result of Shredder calculation, step 3 of 6
```

```
var shred_result_4{MC,SC,LC} >=0 <=1 ; # Result of Shredder calculation, step 4 of 6
var shred_result_5{MC,SC,LC} >=0 <=1 ; # Result of Shredder calculation, step 5 of 6

var x2{MC,SC,LC}>=0 <=1;# Stream x2,  divided into Mineral Class, Size Class and Liberation Class
var x3{MC,SC,LC}>=0 <=1;# Stream x3,  divided into Mineral Class, Size Class and Liberation Class
var y3{MC,SC,LC}>=0 <=1;# Stream y3,  divided into Mineral Class, Size Class and Liberation Class
var x4{MC,SC,LC}>=0 <=1;# Stream x4,  divided into Mineral Class, Size Class and Liberation Class
var x41{MC,SC,LC}>=0 <=1;# Stream x41, divided into Mineral Class, Size Class and Liberation Class
var x42{MC,SC,LC}>=0 <=1;# Stream x42, divided into Mineral Class, Size Class and Liberation Class
var x43{MC,SC,LC}>=0 <=1;# Stream x43, divided into Mineral Class, Size Class and Liberation Class
var y4{MC,SC,LC}>=0 <=1;# Stream y4,  divided into Mineral Class, Size Class and Liberation Class
var x5{MC,SC,LC}>=0 <=1;# Stream x5,  divided into Mineral Class, Size Class and Liberation Class
var x51{MC,SC,LC}>=0 <=1;# Stream x51, divided into Mineral Class, Size Class and Liberation Class
var x52{MC,SC,LC}>=0 <=1;# Stream x52, divided into Mineral Class, Size Class and Liberation Class
var y5{MC,SC,LC}>=0 <=1;# Stream y5,  divided into Mineral Class, Size Class and Liberation Class
var y51{MC,SC,LC}>=0 <=1;# Stream y51, divided into Mineral Class, Size Class and Liberation Class
var y52{MC,SC,LC}>=0 <=1;# Stream y52, divided into Mineral Class, Size Class and Liberation Class
var z5{MC,SC,LC}>=0 <=1;# Stream z5,  divided into Mineral Class, Size Class and Liberation Class
var z51{MC,SC,LC}>=0 <=1;# Stream z51, divided into Mineral Class, Size Class and Liberation Class
var z52{MC,SC,LC}>=0 <=1;# Stream z52, divided into Mineral Class, Size Class and Liberation Class
var x6{MC,SC,LC}>=0 <=1;# Stream x6,  divided into Mineral Class, Size Class and Liberation Class
var x7{MC,SC,LC}>=0 <=1;# Stream x7,  divided into Mineral Class, Size Class and Liberation Class
var y7{MC,SC,LC}>=0 <=1;# Stream y7,  divided into Mineral Class, Size Class and Liberation Class
var x8{MC,SC,LC}>=0 <=1;# Stream x8,  divided into Mineral Class, Size Class and Liberation Class
var x9{MC,SC,LC}>=0 <=1;# Stream x9,  divided into Mineral Class, Size Class and Liberation Class
var y9{MC,SC,LC}>=0 <=1;# Stream y9,  divided into Mineral Class, Size Class and Liberation Class
var z9{MC,SC,LC}>=0 <=1;# Stream z9,  divided into Mineral Class, Size Class and Liberation Class
var x10{MC,SC,LC}>=0 <=1;# Stream x10, divided into Mineral Class, Size Class and Liberation Class
var x12{MC,SC,LC}>=0 <=1;# Stream x12, divided into Mineral Class, Size Class and Liberation Class

var d11>=0 <=1;# Decision Variable D1, Split factor for 1st stream
var d12>=0 <=1;# Decision Variable D1, Split factor for 2nd stream
var d13>=0 <=1;# Decision Variable D1, Split factor for 3th stream
var d21>=0 <=1;# Decision Variable D2, Split factor for 1st stream
var d22>=0 <=1;# Decision Variable D2, Split factor for 2nd stream
var d31>=0 <=1;# Decision Variable D3, Split factor for 1st stream
var d32>=0 <=1;# Decision Variable D3, Split factor for 2nd stream
var d41>=0 <=1;# Decision Variable D4, Split factor for 1st stream
var d42>=0 <=1;# Decision Variable D4, Split factor for 2nd stream

var Aluminium{Pr,MC,SC,LC}>=0 <=1;# Aluminium Product in (5x5x5x5) matrix
var Copper{Pr,MC,SC,LC}>=0 <=1;# Copper Product in (5x5x5x5) matrix
var Steel{Pr,MC,SC,LC}>=0 <=1;# Steel Product (5x5x5x5) matrix
var ASR{Pr,MC,SC,LC}>=0 <=1;# ASR Product (5x5x5x5) matrix
var Rest{Pr,MC,SC,LC}>=0 <=1;# Rest Product (5x5x5x5) matrix

var Products1{Pr,MC,SC,LC}>=0 <=1;# sum of all products into 1 product matrix (5x5x5x5)
var Products2{Pr,MT}>=0 <=1;#sum of all products into 1 product matrix (End Product x Material Type)
var Products3{Pr}>=0 <=1;#sum of all products into 1 product vector (End Product mass distribution)

var MT_Dist{MT}>=0 <=1;# Material Type mass distribution in the input stream

var Grades{MT,Pr}>=0 <=1;#Matrix containing the grades of all Material Types in each End Product (5x5)
var Grade{MT}>=0 <=1;# Vector containing metal grades in their End Product
var Recovery{MT}>=0 <=1;# Vector containing metal recoveries in their End Product


# OBJECTIVE #

maximize Metal_Recovery: sum {e in MT} Recovery[e]*MT_Dist[e] / sum {p in Pr} Matrix_Metal_Streams[p]*
Products3[p] ;

# Objective function, maximizing the total weighted metal recovery

# CONSTRAINTS #

subject to Shredding_step_1{m in MC, e in MT, s in SC}: sum {l in LC} LC_Def[m,l,e] * LC_Dist[s,l]=
shred_result_1[m,e,s];
subject to Shredding_step_2{l in LC}: sum {s in SC} LC_Dist[s,l] * SC_Dist[s] = shred_result_2[l];
subject to Shredding_step_3{m in MC, s in SC, e in MT}: shred_result_1[m,e,s] / ( sum {t in SC}
shred_result_1[m,e,t] )
= shred_result_3[m,e,s] ;
subject to Shredding_step_4{m in MC, s in SC, l in LC}: sum {e in MT} shred_result_3[m,e,s]*LC_Def[m,l,e]=
```

```
shred_result_4[m,s,l];
subject to Shredding_step_5{m in MC, s in SC, l in LC}: shred_result_4[m,s,l]*shred_result_2[l]=
shred_result_5[m,s,l];
subject to Shredding_step_6{m in MC, s in SC, l in LC}: shred_result_5[m,s,l]*MC_Dist[m]= x2[m,s,l];

# Shredding calculations: from data to x2 in 6 steps

subject to Split_i3_x {m in MC, s in SC, l in LC}: x3[m,s,l] = SF_i3_x[s,m] * x2[m,s,l];
subject to Balance_i3 {m in MC, s in SC, l in LC}: x3[m,s,l] + y3[m,s,l] = x2[m,s,l];

# Mass balance over Air Suction, dividing x2 into x3 and y3

subject to Split_i4_x {m in MC, s in SC, l in LC}: x4[m,s,l] = SF_i4_x[m,l] * y3[m,s,l];
subject to Balance_i4 {m in MC, s in SC, l in LC}: x4[m,s,l] + y4[m,s,l] = y3[m,s,l];

# Mass balance over Magnetic Separation, dividing y3 into x4 and y4

subject to Split_i5_x {m in MC, s in SC, l in LC}: x5[m,s,l] = SF_i5_x[s,m,l] * x42[m,s,l] ;
subject to Split_i5_y {m in MC, s in SC, l in LC}: y5[m,s,l] = SF_i5_y[s,m,l] * x42[m,s,l] ;
subject to Balance_i5 {m in MC, s in SC, l in LC}: x5[m,s,l] + y5[m,s,l] + z5[m,s,l] = x42[m,s,l];

# Mass balance over Eddy Current, dividing x42 into x5, y5 and z5

subject to Mixer_1_i6 {m in MC, s in SC, l in LC}: x41[m,s,l]+x51[m,s,l]+y51[m,s,l]=x6[m,s,l];

# Mass balance over Mixer 1, summing x41, x51 and y51 to x6

subject to Split_i7_x {m in MC, s in SC, l in LC}: x7[m,s,l]=SF_i7_x[s,m,l]*x6[m,s,l] ;
subject to Balance_i7 {m in MC, s in SC, l in LC}: x7[m,s,l]+y7[m,s,l]=x6[m,s,l] ;

# Mass balance over Non Ferrous 1, dividing x6 into x7 and y7

subject to Mixer_2_i8 {m in MC, s in SC, l in LC}: x52[m,s,l]+y52[m,s,l]+x43[m,s,l]+z51[m,s,l]=x8[m,s,l];

# Mass balance over Mixer 2, summing x52, y52, x43 and z51 to x8

subject to Split_i9_x {m in MC, s in SC, l in LC}: x9[m,s,l]=SF_i9_x[s,m,l]*x8[m,s,l] ;
subject to Split_i9_y {m in MC, s in SC, l in LC}: y9[m,s,l]=SF_i9_y[s,m,l]*x8[m,s,l] ;
subject to Balance_i9 {m in MC, s in SC, l in LC}: x9[m,s,l]+y9[m,s,l]+z9[m,s,l]=x8[m,s,l] ;

# Mass balance over Non Ferrous 2, dividing x8 into x9, y9 and z9

subject to Mixer3_i10 {m in MC, s in SC, l in LC}: x7[m,s,l]+x9[m,s,l]=x10[m,s,l] ;

# Mass balance over Mixer 3, summing x7 and x9 to x10

subject to Mixer4_i12 {m in MC, s in SC, l in LC}: y7[m,s,l]+y9[m,s,l]=x12[m,s,l] ;

# Mass balance over Mixer 4, summing y7 and y9 to x12

subject to Split_d11 {m in MC, s in SC, l in LC}: d11 * x4[m,s,l] = x41[m,s,l] ;
subject to Split_d12 {m in MC, s in SC, l in LC}: d12 * x4[m,s,l] = x42[m,s,l] ;
subject to Split_d13 {m in MC, s in SC, l in LC}: d13 * x4[m,s,l] = x43[m,s,l] ;
subject to Balance_d1: d11 + d12 + d13 = 1 ;

# Mass balance over Decision Point D1, dividing x4 into x41, x42 and x43

subject to Split_d21 {m in MC, s in SC, l in LC}: d21 * x5[m,s,l] = x51[m,s,l] ;
subject to Split_d22 {m in MC, s in SC, l in LC}: d22 * x5[m,s,l] = x52[m,s,l] ;
subject to Balance_d2: d21 + d22 = 1 ;

# Mass balance over Decision Point D2, dividing x5 into x51 and x52

subject to Split_d31 {m in MC, s in SC, l in LC}: d31 * y5[m,s,l] = y51[m,s,l] ;
subject to Split_d32 {m in MC, s in SC, l in LC}: d32 * y5[m,s,l] = y52[m,s,l] ;
subject to Balance_d3: d31 + d32 = 1 ;

# Mass balance over Decision Point D3, dividing y5 into y51 and y52

subject to Split_d41 {m in MC, s in SC, l in LC}: d41 * z5[m,s,l] = z51[m,s,l] ;
subject to Split_d42 {m in MC, s in SC, l in LC}: d42 * z5[m,s,l] = z52[m,s,l] ;
subject to Balance_d4: d41 + d42 = 1 ;
```

```
# Mass balance over Decision Point D4, dividing z5 into z51 and z52

subject to Aluminium_Product {p in Pr, m in MC, s in SC, l in LC}: Aluminium[p,m,s,l] =
Pr_Matrix_Aluminium[p,m,s,l] * x10[m,s,l];
subject to Copper_Product {p in Pr, m in MC, s in SC, l in LC}: Copper[p,m,s,l] =
Pr_Matrix_Copper[p,m,s,l] * x12[m,s,l];
subject to Steel_Product {p in Pr, m in MC, s in SC, l in LC}: Steel[p,m,s,l] =
Pr_Matrix_Steel[p,m,s,l] * y4[m,s,l];
subject to ASR_Product {p in Pr, m in MC, s in SC, l in LC}: ASR[p,m,s,l] =
Pr_Matrix_ASR[p,m,s,l] * x3[m,s,l] ;
subject to Rest_Product {p in Pr, m in MC, s in SC, l in LC}: Rest[p,m,s,l] =
Pr_Matrix_Rest[p,m,s,l] * ( z52[m,s,l] + ] );
z9[m,s,l] ) ;
# Calculation putting the End Products into their boxes

subject to PRODUCTS1 {p in Pr, m in MC, s in SC, l in LC}: Aluminium[p,m,s,l] + Copper[p,m,s,l] +
Steel[p,m,s,l] + ASR[p,m,s,l] +
Rest[p,m,s,l] = Products1[p,m,s,l] ;
subject to PRODUCTS2 {p in Pr, e in MT}:  sum {m in MC} sum {l in LC} LC_Def[m,l,e] *
sum {s in SC} Products1[p,m,s,l] = Products2[p,e];
subject to PRODUCTS3 {p in Pr}: sum {m in MC, s in SC, l in LC} Products1[p,m,s,l] = Products3[p];

# Calculations for End Products 1, 2 and 3

subject to MT_DIST {e in MT}: sum {m in MC} sum {s in SC} shred_result_1[m,e,s]*SC_Dist[s]*MC_Dist[m]=
MT_Dist[e];

# Calculation for Material Type distribution in input

subject to GRADES {e in MT, p in Pr}: Products2[p,e] / sum {f in MT} Products2[p,f]= Grades[e,p];
subject to GRADE {e in MT}: sum {p in Pr} Matrix_Pr_MT[p,e] * Grades[e,p] = Grade[e] ;
subject to RECOVERY {e in MT}: sum {p in Pr} Products2[p,e] * Matrix_Pr_MT[p,e] / MT_Dist[e]=Recovery[e];

# Calculations for Grades and Recovery

    # Data
```

C.3 Excel optimization model

The Excel files can be found on the included files on the accompanying CD. These Excel optimization models have been developed from the theory presented in Part III. Follow the detail within the cells of the spreadsheet and other comments to run models.

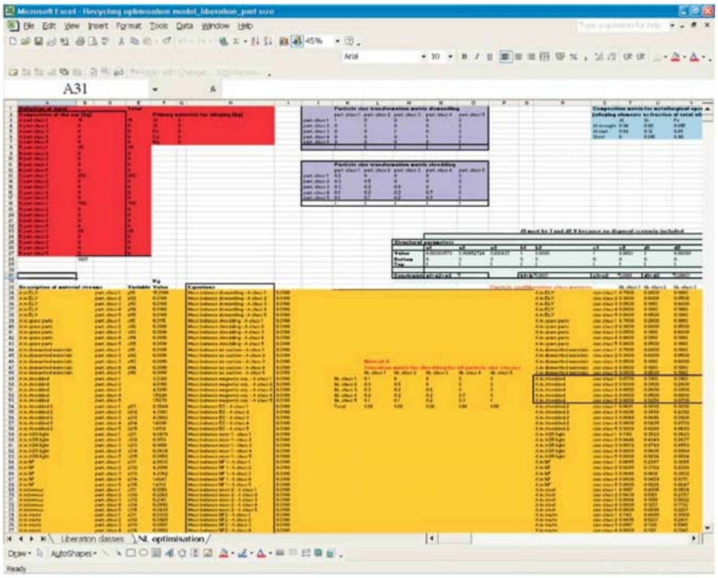
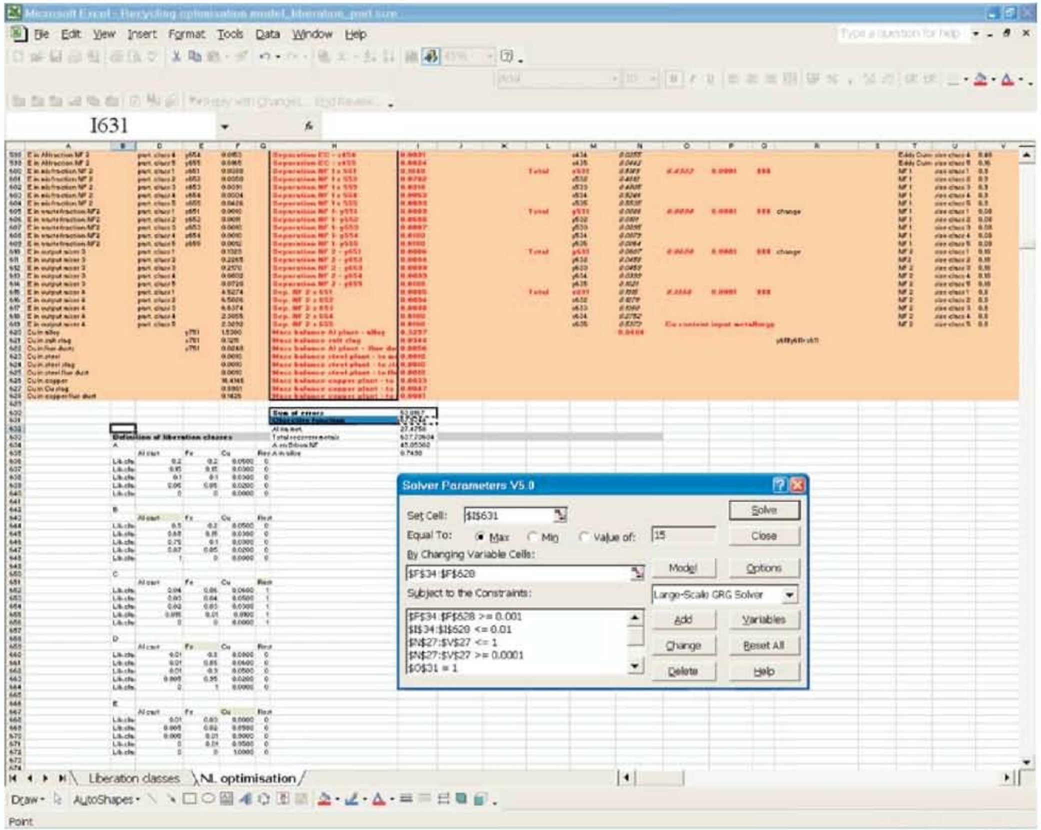


Figure C.1: Screen capture recycling optimisation model liberation/particle size



Set Cell: $I$631

Equal To: ● Max ○ Min ○ Value of: 15

By Changing Variable Cells:

$F$34:$F$628

Subject to the Constraints:

$F$34:$F$628 >= 0.001
$I$34:$I$620 <= 0.01
$N$27:$V$27 <= 1
$N$27:$V$27 >= 0.0001
$O$31 = 1

Large-Scale GRG Solver

Figure C.2: Screen capture recycling optimisation model liberation/particle size (Solver and objective function)

Appendix D

Simulink model for Metal Web

This model may be found on the provided CD rom under the directory **"SIMULINK"**. Copy the files into the mentioned directory in the "Readme.doc" file. This document also provides hints how to run some of the pre-defined scenarios as do various text boxes on the different interfaces of the software.

This model is intended as a training tool only, for the user to adjusted at will, obviously if the model is understood sufficiently well and if the user commands Simulink. The model describes and simulates an extremely complex system and therefore inaccuracies could occur, for which the authors can not be held responsible. However, we would be grateful for feedback. We do, however, urge the users to adapt the software and improve it and perhaps from it could arise a shareware version of this model describing the "Web of Metals". This model provides (among others) the following information :

- various detailed information about the metal producing technology,
- the complex structure of the "Web of Metals",
- the reactor technology within the this web,
- separation data for the reactors, which can be found by exploring the data of each reactor (user must know Simulink well to do this),
- various time-delays and life-times of various products, and
- various pre-defined scenarios in the software, which are also discussed in Part II.

The software can be installed and first simulations can be run by the following procedure, which can also be found in the latest Readme.doc file in the MATLAB directory of the CD rom:

- Install Matlab and Simulink ⟨ Matlab Version 6.1 ⟩
- Copy the model files into the "work" sub-directory of the "MATLAB6p1" directory
- If another directory is used, use the menu item "File / Set Path" to include the directory in the Matlab search path

- Type ⟨MODELname⟩.mdl in the Matlab Command Window to load the model or use "File Open" menu option of Matlab or Ctr+O
- The Simulink model window appears
- Clicking on any model subsystem pops up a window with information about it, or shows the underlying model structure (requires Simulink knowledge)
- Use the information buttons for a quick start
- Brows through the metal life cycles to learn more about the production and recycling processes, by pressing on the different life cycle components
- Load scenario using the Model browser or by clicking the model buttons on the model screen (Example: Load the quasi dynamic scenario that simulates *ceteris paribus* changes in 2000 by pressing subsequently on the ⟨Scenario⟩, ⟨Quasi Dynamic⟩ and ⟨Global GML 2000 - Quasi Dynamic⟩ buttons, and for example turn off ⟨Pb sintering processes⟩ by using the ⟨On⟩ and ⟨Off⟩ buttons below it.)
- Run the scenario through menu option "Simulation" and "Start" of Simulink or by pressing the ¡play¿ button on the Simulink taskbar
- Access simulation results through either Impact Assessment (holistic Eco-Indicator '99 interpretation of results) or Inventory Analysis (detailed, separate flows)
- View process parameters using the the menu option "File" and "Open" in Matlab or Ctr+O to open the corresponding M-file of each process (⟨Metal⟩⟨processname⟩.m)

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